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THE CONTAMINATION-REACTION RULES

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ABSTRACT. A graphical thermodynamic method is used to derive six "contamination-reaction rules." They relate the order of disappearance of phase assemblages to variations of temperature, pressure, and activities of mobile components when compositions change in a particular way.

Thus:

Referring to a particular horizontal row below, let quantities A remain constant. Let a given reactant phase assemblage disappear reversibly with B variation in C to form a product assemblage at a given value of C, C₁. Then the compositional change represented by additional presence of a phase, compatible with the reactant assemblage and incompatible with the product assemblage, causes a shift, D (to C₂), in the condition for reversible disappearance of the contaminated reactant assemblage.

	(A)	(B)	(C)	(D)
1)	n _a , ..., n _e ; a _f ^A , ..., a _k ^A ; P; λ	+	T	T ₂ < T ₁
2)	" ; " ; " ; λ	-	"	T ₂ > T ₁
3)	" ; " ; " ; T; λ	+	P	P ₂ < P ₁
4)	" ; " ; " ; λ	-	"	P ₂ > P ₁
5)	" ; a _f ^A , ..., a _k ^A ; P; T; λ	+	a _f ^A	a _f ^A < a _f ^A
6)	" ; " ; " ; T; λ	-	"	a _f ^A > a _f ^A

NOTATION: n: number of moles; P: pressure; T: temperature; a^A: activity (related to pure component at equilibrium fissure P and T in question); subscripts a to e: fixed components; subscripts f to k: mobile components; λ: ratio between the variations of fluid pressure in the environment and lithostatic pressure.

Application is based on data readily ascertained in field and laboratory. The rules provide one possible analytical basis for the subdivision and arrangement of the mineral facies of rocks. They also emphasize the need for caution in applying results of experimental study of "clean" compositional systems to petrogenetic interpretation.

INTRODUCTION

In one of his most recent discussions of mineral facies, Eskola (1939) has given the following definition:

A rock will belong to a definite facies, which, for an identical bulk composition, manifests an identical mineral composition, its mineral composition varying according to definite laws with changing bulk composition.²

Much recent work, both in the field and laboratory, has been devoted to determination of the variations in the compositions of minerals in rocks and the variations in the nature and proportions of minerals in rocks with changing bulk compositions in various geological environments and simulated geological environments. In some cases, there has been close correspondence between the

¹ The basic idea on which this paper is based (cf. fig. 5) was discussed in a talk entitled: "Some aspects of metamorphic zoning in western New England," delivered on December 13, 1957, at Berkeley during the 10th Annual Technical Conference of the Institute of Geophysics of the University of California. A brief abstract, distributed at the time, was faulty with respect to treatment of the effects of mobile components.

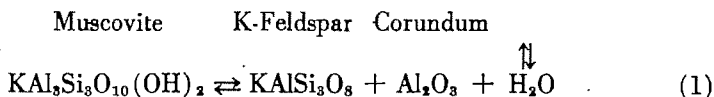
² Free translation.



phase assemblages observed in the laboratory and the mineralogical assemblages found in nature, leading to the conjecture that the laboratory experiments were closely reproducing certain of the critical conditions under which rocks have developed their characteristic mineral assemblages. In other cases the assemblages and, particularly, the *ensembles* (Thompson, 1957, p. 855) of assemblages representing different compositional systems that are observed in the laboratory under specific conditions are sufficiently different from those observed in nature to suggest that there is a considerable dissimilarity between the relevant conditions that resulted in some of the laboratory assemblages and those that resulted in some of the natural occurrences. Parallel to the laboratory studies, there have been theoretical studies, whose goals have been proper elucidation of the "definite laws" to which Eskola referred in the above definition. Notable among these latter studies have been the recent writings of Thompson (1955, 1959, and in press), Korzhinskii (1957), Ramberg (1952), Barth (1952), and Fyfe, Turner, and Verhoogen (1958). The chief goal of this paper lies in this last area of study, where the principal purpose will be the proper formulation from thermodynamics of a series of inequalities relating conditions for chemical reaction in thermodynamic systems (either closed or open) whose compositions are altered in a particular way. The six rules, so deduced, will be called "the contamination-reaction rules." A second purpose will be to examine selected natural occurrences of mineral assemblages and experimental studies in phase equilibria from the standpoint of these rules.

EMPIRICAL BASIS FOR THE ZONING OF METAMORPHIC ROCKS

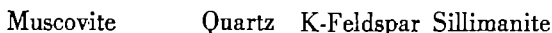
By careful study of areas of igneous and metamorphic rocks geologists are able to accumulate considerable empirical knowledge of mineralogical transformations. As a simple example, in an area of metamorphic rocks, a geologist might note that a given stratigraphic unit in a certain part of an area is characterized by the presence of muscovite. In another part of the same area he might note that muscovite is absent in the same unit, but that an assemblage containing potassic-feldspar and corundum is found instead. From knowledge of the chemical compositions of the minerals observed, he is able to infer that a chemical reaction has taken place approximately in accord with the following chemical equation:



(Note: the system is open to H_2O , a "mobile" (symbolized by: $\updownarrow$) component) or that other reaction has occurred, leading to muscovite in one part of the area and to its compositional equivalent (except for the mobile component, H_2O), potassic feldspar and corundum in another part of the area. If the two parts of the area are in contact with one another, as would commonly be the case, the presumption is that the described reaction has occurred instead of the latter possibility.

By careful petrographic study of the zone of transition, the geologist is commonly able further to adduce textural evidence as to the *direction* in which

the reaction took place and that this direction has commonly been toward the right. Comparison with experimental studies in the same chemical system (Yoder and Eugster, 1955) leads to the conclusion that this reaction, in which a mobile component has been driven off, proceeds to the right with rising temperature. This conclusion is also in accord with the geological evidence that the rocks were originally "cold" in their surface sedimentary environment and that they must have been heated progressively during burial in a manner analogous to the present rise of temperature with depth. Upon further observation within the same area, the geologist might note that the *assemblage*, quartz and muscovite, is more restricted in its areal extent within the zone containing muscovite in quartz-free rocks, and that the area in which the quartz and muscovite coexist is nowhere in contact with the area in which potassic feldspar and corundum coexist. Instead, the former area is in contact with an area in which potassic feldspar and sillimanite coexist and in which muscovite, if present, is in rocks that do not contain quartz. Using reasoning similar to that used above, he infers that the following reaction has taken place with rising temperature toward the right (see Heald, 1950):



With the above information, he would be able to delineate on a metamorphism map of the area two isograds³ separating three zones characterized by three different metamorphic facies. Figure 1 consists of triangular diagrams illustrating the assemblages for the three facies described. Figure 2 is a schematic geologic map showing the occurrence of the phenomena referred to above, the isograds and the defined metamorphic zones. In figure 2 the indicated assemblages may include other compatible phases (e.g. sillimanite in assemblage B).

In summarizing the significance of the information in figure 2, it is important to emphasize that:

- A. Observation of muscovite, without attention to other coexisting minerals, indicates only that the facies is not γ , and, for the simple illustration being considered, must be either α or β .
- B. Observation of the assemblage, muscovite and quartz, indicates that the facies is α .
- C. Observation of the assemblage, potassic feldspar and corundum, indicates that the facies is γ .
- D. Observation of the assemblage, potassic feldspar and sillimanite, indicates that the facies is *not* α and must be either β or γ .

Facies β is defined by the presence in the same restricted locality of assemblages A and D (*not necessarily* in the same rock specimen). Facies β is defined either by the assemblage, A + D or the *ensemble* of assemblages A and D.

Superposition of the three triangular diagrams of figure 1 results in a diagram containing the five areas indicated in figure 3a. The transitions that

³ See subsequent discussion (page 15).

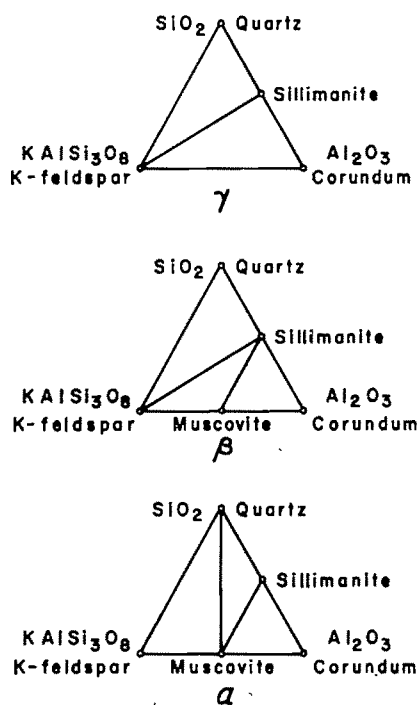


Fig. 1. Associations characteristic of metamorphic facies. See text for explanation.

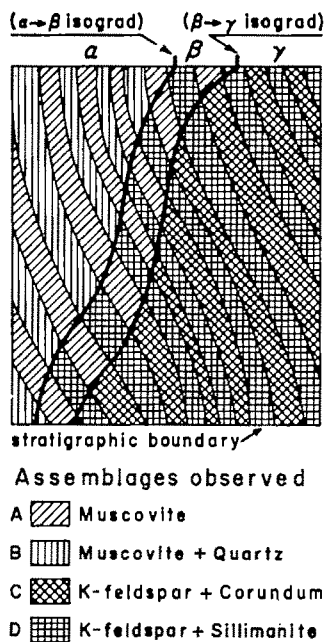
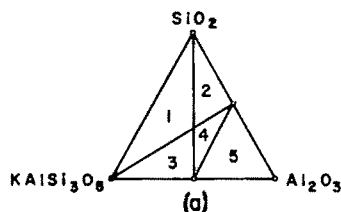


Fig. 2. Schematic geology-metamorphism map. See text for explanation.

occur for compositions within the separate areas are indicated in figure 3b. It is clear that compositional triangles 3 and 4 represent the most desirable compositional ranges, as such rock compositions will reflect both transitions. The finding of a phase assemblage of the proper proportions to lie in the compositional range of these two triangles will give definite indication of the metamorphic zone in which the assemblage occurs.



Phase
Transitions
 $\alpha \rightarrow \beta$ $\beta \rightarrow \gamma$

Compositional Areas	1	X	
	2	X	
	3	X	X
	4	X	X
	5		X

(b)

Fig. 3. Compositional ranges (a) and the transitions indicated within the separate compositional ranges (b). See text.

From knowledge that the metamorphism was progressive (i.e. sequential through the various observable stages) the geologist might feel safe in concluding from spatial relationships that assemblage B of figure 2 was stable over a more restricted range of metamorphic conditions within the area than assemblage A, and that assemblage D preceded C in the area now characterized by the latter (zone γ).

From observation of similar behavior for other compositional systems the geologist might note a seeming general tendency for *diminution of the area of stability of metamorphic mineral assemblages resulting from reaction of these assemblages with "contaminating" minerals*. In reaction (2) above, it is of interest to note that the "contaminating" mineral, quartz, is *consumed* in the reaction involving the phase on the left-hand side of reaction (1). This consumption is represented by the well-known *incompatibility* of corundum and quartz reflected in the stable existence of sillimanite.

THEORY

The above generalization concerning diminution of area of stability of assemblages with "contamination-reaction" gives little indication of the manner in which the causative factors of metamorphism that restrict stability are altered. To obtain a rigorous statement concerning the variations of these factors with "contamination-reaction", it is desirable to look to thermodynamics.

For the purpose of analysis of chemical systems that, as in the above examples, are commonly open to certain mobile components (indicated by subscripts $f, g, \dots, k$), it is desirable to use a thermodynamic potential, still not widely used in theoretical analyses of metamorphic processes, whose variables, for a fixed number of moles of non-mobile components ($n_a, n_b, \dots, n_e$), are temperature (T), pressure (P)⁴, and the *externally* controlled chemical potentials of certain mobile components ($\mu_f, \mu_g, \dots, \mu_k$). In the subsequent development this thermodynamic potential will be referred to as the Korzhinskii-Thompson Function and will be denoted by the letter symbol, L . Korzhinskii appears to have been the first to have defined this function and recognized its importance for the analysis of rock metamorphism (for recent treatment see Korzhinskii (transl.), 1959, p. 20-30). Thompson (1955, p. 80) independently concerned himself with a similar function, obtained by "partitioning" G , the Gibbs Function (cf. "Gibbs free energy"), into that part in the rock and that in the environment. Unaware of Korzhinskii's prior work, he independently considered L in a course given at Harvard University in 1955. In a paper in preparation Thompson (oral communication) makes L more applicable to rock systems by justifying the introduction of activities of mobile components in place of their chemical potentials as the appropriate variables components in place of their chemical potentials as the appropriate variables.

By application of the Legendre transformation to the equation for the internal energy (U), Korzhinskii obtains the new function (L), defined in the following fashion:

$$L \equiv U + PV - TS - \sum_f^k \mu_m n_m = \sum_a^e \mu_i n_i \quad (3)$$

where, in addition to the previously defined terms, V indicates volume, S indicates entropy, and the subscripts m and i refer to mobile components and fixed components respectively such as f and a .

From expression (3), by differentiation and combination with the combined statement of the first and second laws of thermodynamics for chemically variable systems, he obtains the following expression for the variation of the Korzhinskii-Thompson Function:

$$dL = VdP - SdT + \sum_a^e \mu_i dn_i - \sum_f^k n_m d\mu_m - dQ' \quad (4)$$

In this expression the "uncompensated heat", dQ' , is equal to zero for reversible processes, with which this paper is largely concerned. Thus, for reversible processes, expression (4) reduces to:

$$dL = VdP - SdT + \sum_a^e \mu_i dn_i - \sum_f^k n_m d\mu_m. \quad (5)$$

⁴ P stands for "total pressure" or, in metamorphic systems, "lithostatic pressure."

It should be noted that L and dL reduce to G and dG in the absence of mobile components of externally controlled chemical potential. Equation (5) is a "fundamental equation" in the sense of Gibbs (1928, p. 85-89) and is to be regarded as a combined statement of the first and second laws of thermodynamics as applied to a reversible process in a chemically variable system open to certain components of externally controlled chemical potential. For stable chemical equilibrium, the potential, L , will have the lowest possible value when the independent variables in equation (5) are held constant (Korzhinskii, 1959, p. 24-27; see also Zemansky, 1957, p. 414-415, for a method applicable to this case in which the "uncompensated heat" does not appear).

Following up reasoning in an earlier paper (Thompson, 1957, footnote on p. 844), Thompson (in preparation) recasts equation (5) into the following more useful form:

$$dL = (V - \sum_f^k n_m \bar{V}_m^\circ) dP - [S - \sum_f^k n_m (\bar{S}^\circ - R \ln a^\circ)_m] dT \\ - RT \sum_f^k \frac{n_m}{a_m^\circ} da_m^\circ + \sum_i^e \mu_i dn_i. \quad (6)$$

In equation (6) R equals the gas constant; $\bar{V}_m^\circ$ stands for the partial molar volume of the stable form of the particular mobile component in the pure state at the P and T in question; $\bar{S}_m^\circ$ stands for the partial molar entropy under the same conditions; and a_m° stands for the activity of the particular mobile component, defined by the following equation:

$$a_m^\circ \equiv e^{\frac{\mu_m - \mu_m^\circ}{RT}} \quad (7)$$

In (7) μ_m° equals the chemical potential of the pure mobile component in its stable form at the P and T in question.

Following the lead of Thompson (1955, p. 86-88) it would seem that a different definition of activity would provide a more suitable variable for interpreting many geological processes. Let a_m^Δ be an activity defined by the following equation:

$$a_m^\Delta \equiv e^{\frac{\mu_m - \mu_m^\Delta}{RT}} \quad (8)$$

where μ_m^Δ refers to the chemical potential of the particular mobile component in the stable pure form at the T in question and at the P of a fluid in a fissure in chemical equilibrium with the rock.⁵ The superscript, Δ , refers to a property

⁵ For the purposes of this discussion, disequilibria at the fissure walls are being ignored, and these walls are being considered as stable semi-permeable membranes permeable to m . See footnote on page 12. It should be noted that the fluid pressure is a physically measurable pressure and not a "partial pressure."

in the environment. Following a procedure otherwise similar to that used by Thompson (in preparation), the following relation results:

$$\left. \begin{aligned} dL = & VdP - \left(\sum_i^k n_m \bar{V}_m^\Delta \right) dP^f - \left[S - \sum_i^k n_m (\bar{S}^\Delta - R \ln a_i^\Delta) \right]_m dT \\ & - RT \sum_i^k \frac{n_m}{a_m^\Delta} da_m^\Delta + \sum_i^o \mu_i dn_i \end{aligned} \right\} \quad (9a)$$

or

$$\left. \begin{aligned} dL = & (V - \lambda \sum_i^k n_m \bar{V}_m^\Delta) dP - \left[S - \sum_i^k n_m (\bar{S}^\Delta - R \ln a_i^\Delta) \right]_m dT \\ & - RT \sum_i^k \frac{n_m}{a_m^\Delta} da_m^\Delta + \sum_i^o \mu_i dn_i \end{aligned} \right\} \quad (9b)$$

In equations (9a) and (9b) $\bar{V}_m^\Delta$ and $\bar{S}_m^\Delta$ signify the partial molar volume and entropy respectively of the particular mobile component in the stable pure form at the T in question and at the P of a fluid (P^f) in a fissure in chemical equilibrium with the rock. The coefficient λ is defined by the following equation:

$$\lambda \equiv \frac{dP^f}{dP} \text{ or } dP^f = \lambda dP. \quad (10)$$

The principal difference between relations (6) and (9) involves the introduction of the fluid pressure as a variable in (9a). If there is "fissure equilibrium" (Thompson, 1955) the ratio between the variations of lithostatic pressure and fluid pressure (λ) is likely to be constant, thereby justifying the simplification (9b). λ will always have a value equal to or less than 1 for open systems, and, in certain cases, might have a value as low as 0.37, the approximate ratio between the variations of the pressure of a water-filled column and that of an adjacent rock column, both oriented in the same direction. The necessity for considering this factor is indicated by Thompson (1955). In actual cases λ would probably have a value intermediate between a figure of approximately 0.37 and 1. In the case of vertical translation in a rock column adjacent to a water-filled fissure (not necessarily extending to the surface) throughout its length, the former figure would have a greater likelihood (i.e. λ would represent the ratio between the mean densities of the overlying fluid column and the overlying solid column).

From equation (9b) partial differentiation of L with respect to P leads to:

$$\left(\frac{\partial L}{\partial P} \right)_{T; n_s, \dots, n_o; a_i^\Delta, \dots, a_k^\Delta; \lambda} = V - \lambda \sum_i^k n_m \bar{V}_m^\Delta \quad (11a)$$

or

$$= \sum_{I=1}^{XII} \sum_i^o \bar{V}_i - \sum_i^k n_m (\lambda \bar{V}^\Delta - \bar{V})_m \quad (11b)$$

In (11b) the Roman numerals, I, ..., XII identify the various phases and

are used subsequently as superscripts to identify phases; ϕ refers to a particular phase such as I; and $\bar{V}$ stands for the partial molar volume of the indicated component in the indicated phase of the system or in the environment (i.e. $\bar{V}_m^\Delta$). Equation (11a) is most suitable for experimental work. Equation (11b) is given because it gives a better idea of the effect that λ has on the variation of L with P . From equation (11b) it is apparent that reactions in which mobile components are liberated would be favored with rising pressure to the extent that

$$\Delta \left(\frac{\partial L}{\partial P} \right)_{T; n_a, \dots, n_e; a_f^\Delta, \dots, a_k^\Delta; \lambda} < 0 \quad (12)$$

Such would normally be the case for the system if $\sum_i^{\text{III}} \sum_f^k n_m (\lambda \bar{V}^\Delta - \bar{V})_m \neq 0$ for the

state richer in the particular mobile components is less than the same quantity in the state with a lower proportion of the same mobile components. Because of the normally dominant role of mobile components in volume changes in metamorphic rocks and the probability that $\lambda < 1$, one should therefore expect (12) to be true for most transitions. In all first order reactions not involving changes in the proportions of mobile components, (12) is rigorously true (i.e. pressure favors the state of higher density).

From equation (9) partial differentiation of L with respect to T leads to:

$$\left(\frac{\partial L}{\partial T} \right)_{P; n_a, \dots, n_e; a_f^\Delta, \dots, a_k^\Delta; \lambda} = - \left[S - \sum_i^{\text{III}} \sum_f^k n_m (\bar{S}^\Delta - R \ln a^\Delta)_m \right] \quad (13a)$$

or

$$= - \sum_i^{\text{III}} \sum_a^e n_i \bar{S}_i + \sum_f^k \sum_m n_m (\bar{S} - \bar{S}^\Delta + R \ln a^\Delta)_m \neq 0 \quad (13b)$$

In (13b) $\bar{S}$ stands for partial molar entropy. As in the cases of (11a) and (11b), (13a) is more suitable for experimental work; and (13b) is better for explanatory purposes. From equation (13b), the probability that, in the vast majority of cases, $\bar{S}_m \neq \bar{S}_m^\Delta$; the necessity that $R \ln a_m^\Delta \leq 0$; and the probability of a dominant role of liberation of mobile components in causing changes in the right hand side of (13b), it would appear that

$$\Delta \left(\frac{\partial L}{\partial T} \right)_{P; n_a, \dots, n_e; a_f^\Delta, \dots, a_k^\Delta; \lambda} < 0 \quad (14)$$

for most reactions in which mobile components are liberated. Therefore rising temperature should favor the reactions (Thompson, 1957, p. 844). In first order reactions proceeding with rising temperature, (14) is rigorously true if no mobile components are exchanged with the environment (i.e. the assemblage stable at higher temperatures has a higher entropy for a given amount of material).

From equation (9) partial differentiation of L with respect to a_i^A leads to:

$$\left(\frac{\partial L}{\partial a_i^A} \right)_{P, T, n_A, \dots, n_E, a_E^A, \dots, a_K^A; \lambda} = -RT \frac{n_i}{a_i^A} \quad (15a)$$

or

$$= -RT \sum_i^{\text{XII}} \left(\frac{n_i}{a_i^A} \right)^{\phi} \quad (15b)$$

It is clear from equation (15) that increasing a_i^A will favor the state in which n_i increases in one or more of the phases of the system.

Figures 4a, 4b and 4c express schematically the relationships implied by equations (11), (13), and (15) respectively for situations where reversible reaction occurs between assemblages, E and F (i.e. $\Delta L = 0$), involving the corresponding changes on the right sides of the three equations. To the left of T_0 , P_0 , and a_{i0}^A in each case assemblage E will have the lower value for L and will therefore be stable. To the right assemblage F will be stable. In figures 4a and 4b, assemblage E might correspond to an assemblage containing a mobile component, and assemblage F to an assemblage in which the same mobile component had been liberated. In figure 4c the opposite relationship would hold.

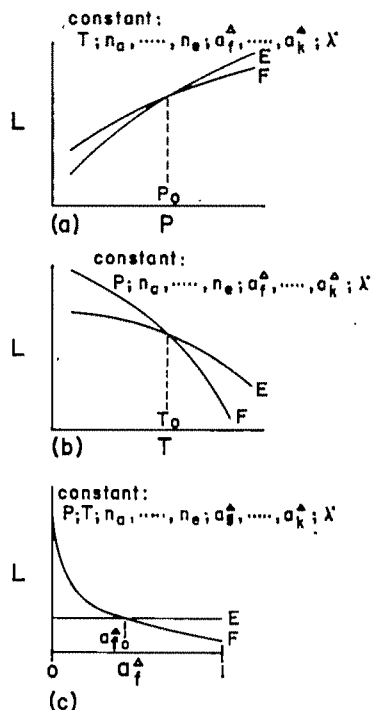
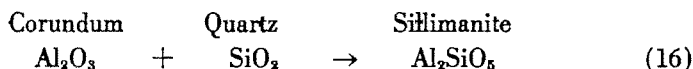
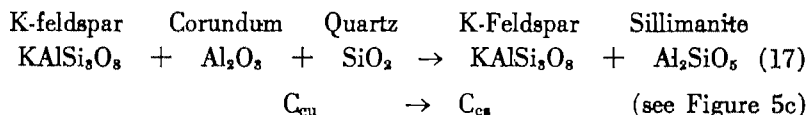


Fig. 4. The Kozhinskii-Thompson Function (L) as a function of temperature (T), pressure (P), and the activities of a mobile component (a_i^A). T_0 , P_0 , and a_{i0}^A correspond to conditions for reversible reaction between phase assemblage E and F (i.e. $\Delta L = 0$). See text.

It is now possible, using schematic illustrations of the type appearing in figures 4a, b and c to deduce graphically from thermodynamics six inequalities that elucidate the generalization on page 5. Let us consider a reaction such as (1), where temperature (T) is the only variable affecting the Korzhinskii-Thompson Function. Figure 5a is the applicable illustration. One mole of $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ in the form of muscovite corresponds to assemblage A, and one mole each of KAlSi_3O_8 and Al_2O_3 in the form of potash-feldspar and corundum, respectively, corresponds to assemblage C. Now, let us imagine the addition to the system under consideration of one mole of SiO_2 in the form of quartz in such fashion that it is kept from reactive contact with the other phases present in the system (for example, it could be sealed in a platinum envelope). The quartz, so added, will have no effect on the temperature of reversible reaction, T_0 (fig. 5a). The only effect it will have is the algebraic increase in the value of L for each of the curves, A and C of figure 5a, to A_c and C_{cu} (fig. 5c), corresponding to the added L value of one mole of SiO_2 in the form of quartz (fig. 5b) at any particular temperature being considered. The addition considered is fundamentally no different from consideration of the inert walls of an experimental bomb as part of a system, something not ordinarily done because the walls usually have little effect on the intensive variables used in describing the behavior of a chemical system under investigation. The condition of reversible reaction ($\Delta L = 0$) will still lie at T_0 after the addition of the molar Korzhinskii-Thompson Function ($L = G$, where no mobile components involved) of SiO_2 in the form of quartz, since both curves A and C rise by the same amount, including their intersection. Now let the added quartz (the contaminant) come into reactive contact with the other phases of the system and observe the effect on the temperature at which reversible reaction takes place. Quartz and muscovite can coexist, so there is no effect on curve A_c (fig. 5c). However, assemblage C_{cu} of figure 5c is unstable, as quartz and corundum will react together irreversibly to form an aluminum silicate (e.g. sillimanite) with a drop in the Korzhinskii-Thompson Function, ΔL . The drop corresponds to the ΔL of the reaction,



which is in turn the same as the drop in L in the reaction,



of figure 5d. The algebraic addition of the curve for ΔL (negative quantity) of figure 5d to the curve for L of assemblage C_{cu} of figure 5c, the unstable assemblage, results in a new curve, C_{cs} , which represents L as a function of T for the stable "contaminated" product assemblage. It is thus seen that the temperature (T_c) for reversible reaction ($\Delta L = 0$) between the reactant assemblage (A_c) and the stable product assemblage (C_{cs}) is reduced relative to T_0 (fig. 5a and c) as a result of the additional presence of a phase (the "contami-

nating" phase) that is compatible with the reactant assemblage and incompatible with the product assemblage at all applicable temperatures. A corollary of the above deduction is that Curve C_{cs} is determined from knowledge of curve C_{cu} and the curve for $\Delta L_{C_{cu} \rightarrow C_{cs}}$ versus temperature (fig. 5d). This derivation presupposes that there exists a temperature range in which the contaminating phase coexists stably with the reactant phases.

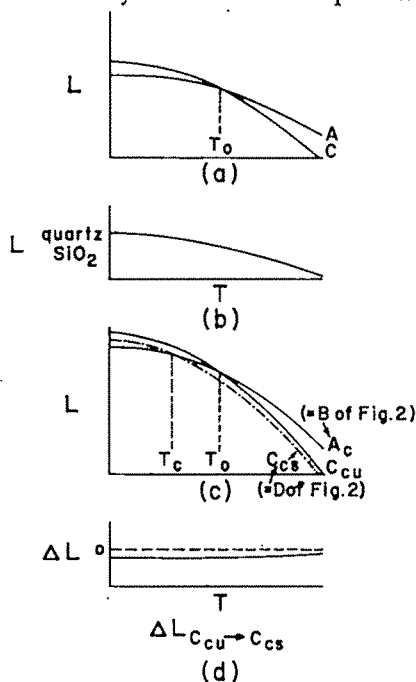


Fig. 5. Graphical demonstration of method for deriving contamination-reaction rules. See text for explanation.

By a similar line of reasoning, using diagrams such as figures 5a, b, and c, it is possible to deduce $(2m + 3)$ other inequalities of similar type (e.g. $T_c < T_0$) involving shifts in the relevant variables of equation (9b)^a to be expected for reversible reaction as a result of the additional presence of a phase compatible with the reactant assemblage and incompatible with the product assemblage. The six types of inequalities, which are here referred to as the "contamination-reaction rules," appear in tabular form in table 1. The derivation above applied to Rule 1 in table 1.

^a Actually there would be $(2m + 5)$ other inequalities if P^* in the environment were allowed to vary independently of P in accord with (9a). The difficulty of visualizing such a physical situation in nature accounts for the writer's reliance on (9b) in spite of the greater mathematical generality of (9a).

The system alone (with constant fixed components), without regard to partition of factors that affect μ_m (or a_m°) in the environment has its state determined by $(m + 2)$ intensive variables (i.e. $P, T, \mu_1, \dots, \mu_x$ or $P, T, a_1^\circ, \dots, a_x^\circ$), leading to $(2m + 4)$ contamination-reaction rules based on equation (6). These $(2m + 4)$ rules were discussed by the writer at the annual meeting of the Geological Society of America in November, 1959 (Rosenfeld, 1959). If one wishes to avoid consideration of a model for the environment, contamination-reaction rules based on (6) are applicable.

TABLE 1^{*}

Referring to a particular horizontal row below, let quantities A remain constant. Let a given reactant phase assemblage disappear reversibly with B variation in C to form a product assemblage at a given value of C, C₁. Then the compositional change represented by additional presence of a phase, compatible with the reactant assemblage and incompatible with the product assemblage, causes a shift, D (to C₂), in the condition for reversible disappearance of the contaminated reactant assemblage.

	(A)	(B)	(C)	(D)
1)	n _a , ..., n _e ; a _r ^A , ..., a _k ^A ; P; λ	+	T	T ₂ < T ₁
2)	" ; " ; " ; λ	-	"	T ₂ > T ₁
3)	" ; " ; T; λ	+	P	P ₂ < P ₁
4)	" ; " ; " ; λ	-	"	P ₂ > P ₁
5)	" ; a _r ^A , ..., a _k ^A ; " ; P; λ	+	a _r ^A	a _{rx} ^A < a _{ri} ^A
6)	" ; " ; " ; λ	-	"	a _{rx} ^A > a _{ri} ^A

NOTATION: n: number of moles; P: pressure; T: temperature; a^A: activity (related to pure component at equilibrium fissure P and T in question); subscripts a to e: fixed components; subscripts f to k: mobile components; λ: ratio between the variations of fluid pressure in the environment and lithostatic pressure.

APPLICATION

Perhaps the greatest utility of the contamination-reaction rules lies in the facility with which they enable one to predict the order in which certain reactions, related by the contamination-reaction rules, would occur with respect to variation of some intensive variable when there is knowledge of the reactions and the accompanying changes in the quantities in column C of table 1. Thus, for example, certain approximate reactions of aluminous rocks, characterized by loss of H₂O, appear in table 2. They can be unscrambled into their order of rising temperature, assuming this to be the chief variable affecting the mineral associations. In table 2, the reactions run with rising temperature reversibly to the right. The incompatible phases are indicated with arrows

^{*} Dr. Hugh Greenwood of the Geophysical Laboratory kindly suggested to the writer a logically compact way in which the content of the rules of table 1 may be expressed in half as many rules. From examination of table 1 it is clear that the even-numbered rules are cognate to the subsequent odd-numbered rules. They are linked by their signs. For example, referring to figure 5c, let T_x be some temperature satisfying the incompatibility condition stated in the following fashion:

$$|L_{Ac} - L_{Cu}| < |L_{Ac} - L_{Cs}| \quad (i)$$

It is then clear that rules 1 and 2 are encompassed in the following generalization:

$$|T_x - T_o| < |T_x - T_c| \quad (ii)$$

Similarly, where the subscript, x, signifies a value for P or a_r satisfying (i), rules (3) and (4) are encompassed by the following statement:

$$|P_x - P_o| < |P_x - P_c| \quad (iii)$$

and rules (5) and (6) are encompassed by the following statement:

$$|a_{rx}^A - a_{ro}^A| < |a_{rx}^A - a_{rc}^A| \quad (iv)$$

The writer prefers the language of table 1 for the statement of the rules, however, because it avoids the introduction of the extra thermodynamic notation of the derivation. Many geologists, familiar with the compatibilities and incompatibilities of minerals in rocks but unfamiliar with thermodynamics, will possibly prefer the rules as stated in table 1. Those familiar with thermodynamics might prefer a form in accord with this footnote.

pointing toward the stable products. In western New England the writer has observed assemblages characteristic of both sides of reactions 2, 3, 4 and 5 of table 2. Independent evidence, such as the narrowing of the miscibility gap between calcite and dolomite and that between paragonite and muscovite, supports the conclusion that reactions 3, 4 and 5 occurred in the order of decreasing temperatures (Rosenfeld and Cotter, 1958; Rosenfeld, Thompson, and Zen, 1958). The relationship between reactions 4 and 5 might account in one way for the fact that the staurolite isograd in some areas of regional metamorphism is "downgrade" from the kyanite isograd. An alternate way of accounting for this last phenomenon lies in the commonly observed incompatibility of chloritoid and kyanite, with staurolite the stable equivalent. Chloritoid has also been observed in association with the minerals on the left side of reaction 5. Using the contamination-reaction rules it is possible to make many other lists of reactions in the order of variation of one of the critical variables, T, P, or $a_{\text{H}_2\text{O}}$, once the critical variable is postulated or determined on other grounds.

TABLE 2
Approximate reactions in order of decreasing temperature
at constant P, $a_{\text{H}_2\text{O}}$, λ :

- (1) $\text{Mu} \rightleftharpoons \text{Ksp} + \text{Cdm} + \text{H}_2\text{O}$
incompatibility: $\text{Qu} + \text{Cdm} \rightarrow \text{Sil}$
- (2) $\text{Mu} + \text{Qu} \rightleftharpoons \text{Ksp} + \text{Sil} + \text{H}_2\text{O}$
incompatibility: $\text{Pa} + \text{Ksp} \rightarrow \text{Mu} + \text{Ab}$
- (3)* $\text{Mu} + \text{Qu} + \text{Pa} \rightleftharpoons \text{Mu} + \text{Ab} + \text{Ky} + \text{H}_2\text{O}$
incompatibility: $\text{Ab} + \text{Py} \rightarrow \text{Pa} + 4\text{Qu}$
- (4) $\text{Mu} + \text{Qu} + \text{Pa} + \text{Py} \rightleftharpoons \text{Mu} + \text{Pa} + 4\text{Qu} + \text{Ky} + \text{H}_2\text{O}$
incompatibility: $4\text{Il} + 9\text{Ky} + \text{H}_2\text{O} \rightarrow 2\text{St} + 4\text{Ru} + \text{Qu}$
- (5)* $\text{Mu} + \text{Qu} + \text{Pa} + 9\text{Py} + 4\text{Il} \rightleftharpoons \text{Mu} + \text{Pa} + 29\text{Qu} + 2\text{St} + 4\text{Ru} + 17\text{H}_2\text{O}$

Mu = Muscovite = $\text{KAl}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$

Ksp = K-feldspar = KAlSi_3O_8

Cdm = Corundum = Al_2O_3

Qu = Quartz = SiO_2

Sil = Sillimanite = Al_2SiO_5

Pa = Paragonite = $\text{NaAl}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$

Ab = Albite = $\text{NaAlSi}_3\text{O}_8$

Ky = Kyanite = Al_2SiO_5

Py = Pyrophyllite = $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$

Il = Ilmenite = FeTiO_3

St = Staurolite = $\text{Fe}_2\text{Al}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$

Ru = Rutile = TiO_2

* Because of the incompatibility: $\text{Qu} + \text{Cdm} \rightarrow \text{Ky}$, it makes no difference in the present treatment if Ky is substituted for Sil in (2). The reaction: $\text{Ky} \rightleftharpoons \text{Sil}$ commonly occurs between (2) and (3).

* The evidence for the incompatibility of Il and Ky appears to be geographically more restricted than evidence for the other incompatibilities listed (kindly brought to my attention by Mrs. E. B. Knopf).

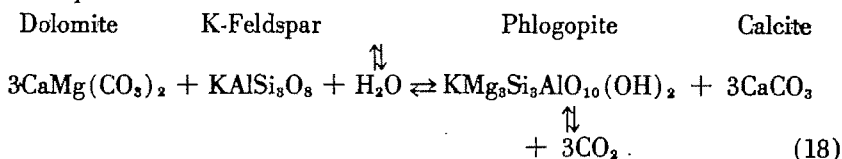
Thus, the contamination-reaction rules can be used to establish qualitatively in their proper relationship to one another $(m + 1)$ - dimensional boundaries, corresponding to reversible reactions, in a "petrogenetic grid" (Bowen, 1940) in $(m + 2)$ - dimensional space, measured by the activities of mobile components (m = number of mobile components which enter or leave the system in the particular reaction) (see footnote 6), temperature, and pressure. The appearance of such an $(m + 1)$ - variant boundary on the surface of the Earth is an isograd, its extension in depth comprising an isogradic surface. The mineral facies are then to be equated to the $(m + 2)$ - dimensional (i.e. $(m+2)$ - variant) regions delineated by these boundaries (Thompson, 1955, p. 66). Two small volumes of rock, each embracing a sufficiently varied ensemble of rock compositions to possess the mineral assemblages critical to a facies, so defined (Thompson, 1957, p. 855), may be said to be isofacial and to lie in the same metamorphic zone in conventional space. The present confused status of the classification of many of the principal mineral facies (and isograds) lies largely in disagreement as to what reactions are to be chosen as boundaries and, in many cases, failure to choose specific reactions as boundaries. Current definitions of individual facies exclude, by their restrictions, the classification of sizeable areas of metamorphic rocks. The multi-dimensional aspect of the problem of such classification has not made the task a simple one and has accounted for recent efforts to work with compositional systems in which mobile components are not exchanged with the environment in the reactions and therefore have no effect on the equilibria (e.g. miscibility gaps, polymorphic transitions, "dry" chemical reactions such as the reaction in which albite transforms into the assemblage, jadeite-quartz). It is hoped that the contamination-reaction rules will prove of some use in defining the boundaries eventually to be adopted.

An interesting possible application of the contamination-reaction rules appeared in a current study in which the writer and others have been engaged (Rosenfeld, Thompson, and Zen, 1958). X-ray measurement of $(c/2) \sin \beta$ spacings (i.e. $d_{(002)}$) of a number of specimens of coexistent paragonite and muscovite from quartz-bearing schists in western New England demonstrated a pronounced narrowing of the miscibility gap with "rising metamorphic grade" (presumably rising temperature). At maximum closure (Gassetts in the town of Chester, Vermont) the "d" spacings are: muscovite, 9.918 Å; paragonite, 9.640 Å. At "higher grades" the assemblage, kyanite and/or sillimanite and sodic plagioclase, appears in place of the assemblage, paragonite and quartz; and muscovite becomes less sodic ("d" spacings become larger). However, in quartz-free kyanite-staurolite schist from the summit of Pizzo Forno in the Swiss Alps,⁸ the miscibility gap between muscovite and paragonite (as evident from "d" spacings) shows considerably greater narrowing than that observed for the same pair of minerals at their "peak grade" in quartzose rocks from western New England. Corresponding "d" spacings at Pizzo Forno are: muscovite, 9.888 Å; paragonite, 9.647 Å. The deficiency of SiO_2 , reflected in the absence of quartz, represents one possible explanation for the extension of the stability of paragonite to a considerably higher temperature than might

⁸ Specimen collected by J. B. Thompson, Jr.

otherwise be the case, (another possibility: high $a_{H_2O}^A$).⁹ The range of the paragonite-muscovite "geothermometer" could be extended by this means into temperature ranges where it ordinarily cannot be used (actually the association represents bivariant equilibrium, for which the pressure effect is probably slight). Further, since the assemblage, paragonite-muscovite, is a "dry" thermometer (i.e. H_2O is not exchanged with the environment in the miscibility reactions), the range of muscovite-paragonite thermometry in which one may ignore the activity (a^A) of the mobile component, H_2O , or "fluid pressure" could be extended. Thus, it is possible to make use of the contamination-reaction rules in searching for material to enable extension of the range of certain types of miscibility gap thermometry to higher temperature conditions than would otherwise be the case. The upper limit of the above thermometer as a bivariant instrument would be determined by the decomposition of one of the dioctahedral micas (normally paragonite) to form corundum and a corresponding feldspar. Unless this last assemblage is found in a given area, there remains the possibility of finding the paragonite-muscovite pair, given sufficient variation in rock composition. The corresponding high temperature limit on the calcite-dolomite geothermometer would be determined by the breakdown of dolomite to give calcite and periclase (or brucite).

The contamination-reaction rules also suggest ways of extending the range of rock compositions that can be used for miscibility gap thermometry at relatively low temperatures. Let us suppose that there is an area occupied by rocks of varying degrees of metamorphism among which dolomitic strata are present. The absence of calcite from such strata would preclude their use for miscibility gap thermometry. However, by appropriate contamination with a mineral capable of reacting under conditions of rising T with part of the dolomite and producing calcite as a byproduct of reaction, it would be possible to use such strata. The occurrence of scattered sand grains of potassic feldspar is common in dolomites. A commonly observed reaction in the lower grades of metamorphism is:



Thus, the absence of calcite from rocks containing dolomite in the low "grade" part of an area need not preclude the use of such rocks for calcite-dolomite geothermometry at slightly higher "grades" of metamorphism if such "contaminant" phases are present to allow "dedolomitization" reactions. It is also commonly possible to achieve such contamination effects at the contacts of otherwise clean dolomite strata with other types of rocks. Calcite produced by reactions such as (18) could conceivably represent equilibrium under conditions of metamorphism more nearly than calcite of sedimentary origin.

* Since this was written the writer has checked d_{000} on muscovite in contact with quartz in another specimen collected by Thompson from the summit of Pizzo Forno. The d_{000} spacing is not materially different from that mentioned above, indicating that the contamination-reaction rules do not account for this particular extension of temperature range.

The contamination-reaction rules provide some insight into certain processes related to the genesis of igneous rocks. Let us imagine the passage of a granitic magma in equilibrium with contained quartz crystals, into a stratum containing dolomite, a phase incompatible with quartz under conditions attendant on intrusion. The presence of such an incompatible phase (e.g. dolomite) would result in a metasomatic reaction in which the components with which the magma is saturated (e.g. SiO_2) would react with the incompatible phase to form a mineral or mineral assemblage (e.g. diopside) compatible with both the magma and the stratum containing the incompatible phase. Such a process would, of necessity, have as a result the modification, by subtraction, of the composition of the magma (e.g. desilication). Such a mechanism might conveniently explain the muscovite-rich zones along the borders of certain granitic pegmatites in sillimanite-bearing schists in western New England. The presumed incompatibility would be between the potassic feldspar and the sillimanite in accord with reaction 2 of table 2. Examples of such metasomatism have been considered recently by Thompson (1959) in a theoretical treatment of the subject.

Consideration of the contamination-reaction rules introduces qualifications concerning interpretations of the stability ranges of certain minerals in igneous rocks. In two recent papers on the synthesis of micas (Yoder and Eugster, 1954, 1955), the writers interpreted the stability ranges of both phlogopite and muscovite in granite by superimposing the decomposition curves (" $P_{\text{H}_2\text{O}}$ ", T) for these synthetic minerals on the minimum melting curves for synthetic "granite" (see fig. 6) of Tuttle and Bowen. Considerable importance is at-

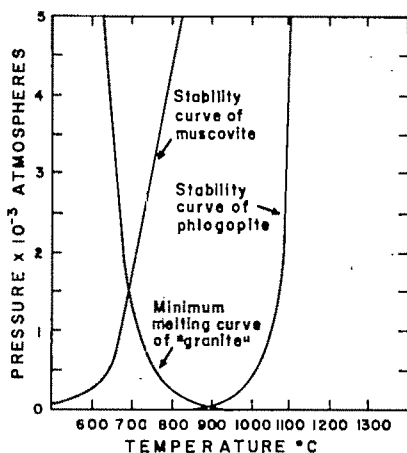


Fig. 6. Minimum melting curve of "granite" superimposed on decomposition curves of muscovite and phlogopite (after Bowen and Tuttle, 1952; and Yoder and Eugster, 1954, 1955).

tached to the intersections of the "granite" curve with the two mica curves. The writers say: "Above approximately 1500 atmospheres (pressure at intersection)¹⁰ it is possible for muscovite to form on the liquidus surface of the

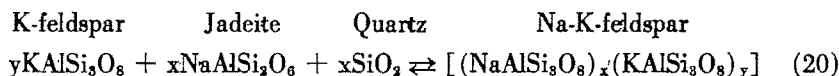
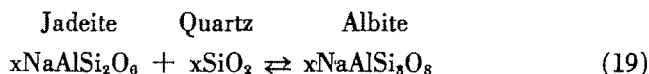
¹⁰ Parentheses added.

'granite' system." They infer from the phlogopite data that a mica of the biotite group "should be found on the liquidus surface of the granite system" at pressures above 60 atmospheres (pressure at intersection.) The minimum melting liquid of granite is capable of stable coexistence with quartz and is therefore saturated with regard to SiO_2 . In both experimental reactions involving the decompositions of micas, the products contain phase assemblages that are incompatible with quartz (i.e. corundum, leucite, forsterite, kalsilite). Therefore, in accord with the contamination-reaction rules, such micas coexisting with the above minimum melting liquid would decompose at lower temperatures. Intersections of the above type would shift to higher pressures. Because of the low angle of intersection of the two curves in the case of muscovite, the increase in the pressure of the intersection might be quite large (it would be amplified to the extent that $a_{\text{H}_2\text{O}}^A < 1$). It is conceivable that the increase might be sufficient to rule muscovite out completely as a primary product of crystallization from the silicate-rich liquid leading to magmatic granites.

In the preceding application of the contamination-reaction rules, emphasis has been placed on changes of a particular intensive variable, characterizing reversible reaction, that represent a definite interval, regardless of the *proportion* of the contamination. The rules can also be applied in cases where a contaminating phase, compatible with a reactant assemblage, is incompatible with an assemblage containing a product phase that can show a *variation* in composition as a result of the contamination-reaction. In fact, it is just such an application that is most familiar. For example, ice melts at 0° centigrade to form water. Ice is compatible with the phase, halite (NaCl). Halite is incompatible with pure water and is capable of dissolving to form saline solutions of varying concentration in which the "free energy" drop (ΔL) would be a function of the proportion of NaCl entering solution. Therefore, since the melting reaction proceeds with rising temperature, the temperature at which "melting" occurs would be lowered increasingly as a result of increasing contamination of the assemblage, with the limiting depression occurring at that concentration for which the product assemblage (the solution) is capable of stable coexistence with halite (i.e. it is saturated) and ice (at the eutectic). By similar reasoning, the elevation of the boiling point of water, with the addition of salt, can be explained in accord with rule 2 of table 1, since the salt dissolves primarily in the liquid phase.

Examples of the application of the rules, in cases involving a continuous variation of concentration in a product phase of the component identified with a reactant phase, occur in connection with the "jadeite problem." Recently there have been attempts to relate the experimental data for the compositional system, $\text{NaAlSi}_2\text{O}_6\text{-SiO}_2$ (Birch and LeComte, 1958), to the problem of the occurrence of eclogite and related geophysical problems (for a stimulating article see: Lovering, 1958). In general a reaction involving the production of pure jadeite would take place at a higher pressure in albitic rocks containing quartz than in rocks containing phases incompatible with quartz, in accord with rule 3 of table 1. This might explain some occurrences of jadeite near

peridotites and serpentinites. The additional presence of K-feldspar would further boost the pressure at which the dense phase, jadeite, would be produced (rule 3, table 1).¹¹ Thus:

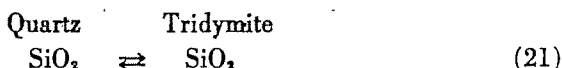


The well-known tendency toward closure of the miscibility gap in the alkali feldspars manifests itself in the elevation of pressure for reaction (20) relative to (19). On the contrary, the assemblage, diopside-hedenbergite and albite, would decompose to form omphacite and quartz at a lower pressure than (19) in accord with rule 4 of table 1. The addition of olivine would further decrease the reaction pressure for omphacite production because of its incompatibility with quartz. From the point of view of this paper one might expect the formation of jadeitic pyroxene at considerably lower pressures in undersaturated nepheline-olivine basalts than in rock of granitic composition. The general absence of such pyroxene in rocks of granitic character suggests that pressures, sufficient to cause formation of such pyroxene in granitic rocks, have rarely, if ever, occurred within the areas in which granitic rocks are exposed in the Earth's crust.

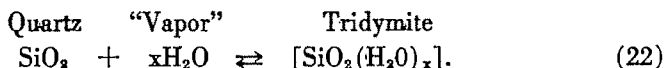
Numerous recent studies have concerned themselves with the stability ranges of the so-called "silica minerals." Apparent inconsistencies have appeared among the results of different investigators who followed different procedures. For example, in a recent review article, Roy and Tuttle (1956, p. 151) point out that the experimental P-T curve for the quartz-tridymite transition determined under *hydro-thermal conditions*, is about four times as steep (relative to the temperature axis) as that calculated from thermochemical data by Mosesman and Pitzer (1941). There has been a tendency to interpret the experimental curve of Tuttle and England (1955), indicating lower transition temperatures, as "correct" and the curve of Mosesman and Pitzer as "wrong" (for example, see Mason, 1958, fig. 16, p. 98). It is possible that recent interpretations, such as the one mentioned above, are based on inadequate formulation of the problem. The work of Mosesman and Pitzer related to an essentially one-component compositional system (SiO_2), and the work of Tuttle and England applied to an essentially two-component compositional system (SiO_2 - H_2O). Buerger (1954) has emphasized that natural tridymite, because of its open framework structure, is commonly a "complex-stuffed" compound. In such cases, it is not related to quartz by polymorphic transition. It would seem quite plausible, in accord with Buerger's treatment, to expect H_2O to concentrate increasingly in tridymite relative to coexisting quartz at increasingly elevated pressures on a coexisting water-rich fluid phase. If such is the case,

¹¹ This example was called to the writer's attention by J. B. Thompson, Jr.

then the apparent paradox mentioned by Roy and Tuttle might be resolved in accord with rule 1 of table 1. Thus,

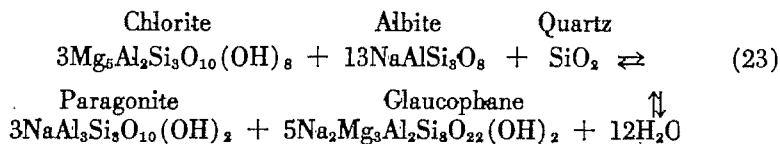


and at a lower temperature,



Clarification of the experimental results of Tuttle and England awaits the determination of the H_2O content of the solid phases under the conditions of equilibrium. It is also possible that the above experimental data might apply to the "dry" system, as there are considerable uncertainties in the thermochemical data.

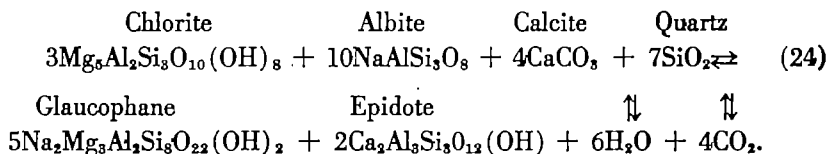
The implications of the discovery of the assemblage, glaucophane-paragonite (see Harder, 1956, p. 251) seem generally to have been insufficiently appreciated in treatments of the problems connected with the subdivision of the glaucophane schist facies. A cursory petrographic examination of glaucophane-bearing rocks from California in the U.C.L.A. collections demonstrates that these rocks span in composition a large portion of the pelitic rock compositions on which the classical grade subdivision of Barrow rests and a large portion of the mafic rock compositions on which Eskola based his facies classification.¹² Generally, however, reactions in the mafic rocks have been emphasized to the neglect of those in the pelitic rocks. This emphasis has disadvantages, as has been indicated by Thompson (1957; in press), inasmuch as the reactions in the mafic rocks commonly involve an exchange of CO_2 with the environment in addition to H_2O , thereby increasing the number of variables affecting the reactions (i.e. $(m+2)=4$). This disadvantage is minimized for reactions in the pelitic rocks, where H_2O is normally the only mobile component exchanged with the environment. An approximate reaction, suggested by the paragonite-glaucophane assemblage, that might serve as an approximate boundary (bivariant) between a common assemblage of the classical "Dalradian"-type metamorphism and one within the "glaucophane schist facies," is the following, which probably proceeds to the right with increase in T and P and decrease in $a_{\text{H}_2\text{O}}$ (see discussion on page 8 et seq.):



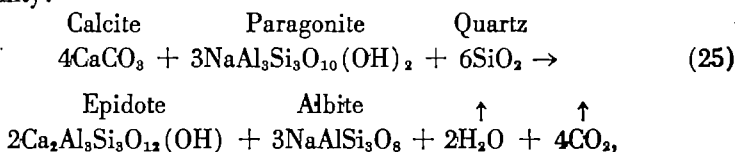
Because of the tendency toward extensive solid solution between muscovite and paragonite, the additional presence of muscovite on the left side of (23) would be expected to cause extension of the range of conditions for the analogous glaucophane-producing reaction in the direction of lower T and P and higher $a_{\text{H}_2\text{O}}$.

¹² They are *not* necessarily hypersodic, as is commonly stated.

Another assemblage that is fairly common, especially in the mafic rocks, in the lower grades of "Dalradian"-type metamorphism, is chlorite-albite-calcite-quartz. In areas characterized by the presence of glaucophane (cf. Anglesey, Wales), it is not unusual to find the association, glaucophane-epidote. A conceivable approximate boundary reaction would be:



This reaction, as in the case of (23), would presumably be favored by elevation of T and P and depression of $a_{\text{H}_2\text{O}}^A$, $a_{\text{CO}_2}^A$ and P^F . Further, in accord with the contamination-reaction rules, the extension of the stability field of the assemblage on the right side of (24) would tilt toward lower T and P and higher $a_{\text{H}_2\text{O}}^A$ at constant $a_{\text{CO}_2}^A$ and λ than in the case of the right side of reaction (23), assuming quartz to be present. This would presumably result from the incompatibility:



an incompatibility the writer has observed at the contacts of paragonitic schist and marble within the "garnet zone" in southeast Vermont.

Both reactions (23) and (24) might be favored strongly in the vicinity of a peridotite by increase of P and T consequent on the expansion and heat production due to serpentinization or steatization, and the decrease in $a_{\text{H}_2\text{O}}^A$ and $a_{\text{CO}_2}^A$ resulting from the same reaction (also the reduction in P^F). Interestingly, a common type of occurrence of glaucophane schists is in the vicinity of serpentinite. Each factor would appear to be more nearly favorable in such an area for reaction toward the right in the cases of (23) and (24). Thompson (1955, p. 99) has considered the possibilities of desiccation in such environments.

SUMMARY

In summary, the contamination-reaction rules represent one possible tool for classifying and interpreting natural phase assemblages in regard to conditions of occurrence. They also suggest potential new sources of information in nature. In regard to experimental petrology, they represent a plea for the experimental study of "dirty" compositional systems more nearly like those that resulted in the rocks we observe. They suggest that there are severe limitations to the utilization of the results of study of many "clean" systems for interpretations of natural assemblages. The roots of the contamination-reaction rules in field observations and in the first and second laws of thermodynamics give the above plea added force.

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CONTROL OF CARBONATE SOLUBILITY BY CARBONATE COMPLEXES*

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ABSTRACT. Activity coefficients of HCO_3^- and CO_3^{--} were determined in aqueous solutions of NaCl , MgCl_2 , and of NaCl-MgCl_2 mixture of approximately the same mol ratio as sea water. The values obtained in "synthetic sea water" correspond to those observed in actual sea water.

The data for CO_3^{--} are interpreted in terms of two complexes:

$$\frac{a_{\text{Mg}^{++}} a_{\text{CO}_3^{--}}}{a_{\text{MgCO}_3^0}} = 4.0 \times 10^{-4}$$

$$\frac{a_{\text{Na}^+} a_{\text{CO}_3^{--}}}{a_{\text{NaCO}_3^-}} = 5.4 \times 10^{-3}$$

Calculations show that of the total CO_3^{--} in sea water, as determined by titration and not including HCO_3^- , about 75 percent is MgCO_3^0 , 15 percent NaCO_3^- , and 10 percent free CO_3^{--} .

The data for HCO_3^- also indicate the presence of complexes of Na^+ and Mg^{++} , but these are less strongly associated, and are not fully characterized.

It is shown that the concentration of Ca^{++} , in equilibrium with calcite, is greater in "synthetic sea water" than in Mg -free NaCl solutions. The observed apparent supersaturation of sea water in calcite is not fully explained here. Although the total concentration of CO_3^{--} in sea water can be predicted from these data, that of Ca^{++} cannot.

INTRODUCTION

It has long been known that the activity of CO_3^{--} in sea water is a small fraction of its molality. Sverdrup (1942, p. 205) gives the activity coefficient γ , ($a_{\text{CO}_3^{--}}/m_{\text{CO}_3^{--}}$), as 0.019. This value of $\gamma_{\text{CO}_3^{--}}$, far less than that expected simply on the basis of electrical effects among ions, can be attributed to the formation of complexes. A brief survey of the literature will serve to show that although complexing of CO_3^{--} was suggested at least as long ago as 1932, and definitely established in 1941, yet more recent papers on the subject tend to neglect the concept. Greenberg and Moberg (1932) suggested the formation of complex molecules or ions between the divalent elements in sea water and the carbonates. In a later paper discussing the buffer mechanism of sea water (Moberg, et al., 1934) the suggestion is repeated that the much lower activity coefficient of CO_3^{--} in sea water than in salt solutions is probably attributable to the divalent ions, Mg^{++} , Ca^{++} , and SO_4^{--} , occurring in sea water. They quote, however, another paper on the same subject (Buch, et al., 1932) in which the suggestion is considered superfluous, and the inter-ionic attraction of completely ionized electrolytes considered sufficient explanation.

There the matter rested, apparently, until Greenwald (1941) showed that both Ca^{++} and Mg^{++} interact with HCO_3^- and CO_3^{--} to form soluble com-

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plexes. Working with solutions of low and nearly constant ionic strength ($\mu = 0.15$), he concluded that the following equilibria exist at 22°:

$$\begin{aligned}\frac{m_{\text{Ca}^{++}} m_{\text{HCO}_3^-}}{m_{\text{CaHCO}_3^+}} &= K'_{\text{CaHCO}_3^+} = 1.6 \times 10^{-1} \\ \frac{m_{\text{Mg}^{++}} m_{\text{HCO}_3^-}}{m_{\text{MgHCO}_3^+}} &= K'_{\text{MgHCO}_3^+} = 1.7 \times 10^{-1} \\ \frac{m_{\text{Ca}^{++}} m_{\text{CO}_3^{--}}}{m_{\text{CaCO}_3^0}} &= K'_{\text{CaCO}_3^0} = 1 \times 10^{-8} \\ \frac{m_{\text{Mg}^{++}} m_{\text{CO}_3^{--}}}{m_{\text{MgCO}_3^0}} &= K'_{\text{MgCO}_3^0} = 4.3 \times 10^{-3}\end{aligned}$$

As far as we are aware, Greenwald's contribution has been generally ignored. Sverdrup (1942) repeats that complexing of CO_3^{--} has been suggested to explain its low activity. In a more recent text (Harvey, 1957) it is stated that the solubility of calcite is greatly increased by the presence of neutral salts (p. 133) and later (p. 166), that neutral salts in the sea water permit the formation of complexes, but no details are given. Revelle and Fairbridge (1957) discuss the relations between carbonates and carbon dioxide, and calcite solubility in sea water, but not from the point of view of complex formation. Hood, Park, and Smith (1959) investigated the calcium carbonate solubility equilibrium in sea water, but not the formation of inorganic complexes of CO_3^{--} .

Greenwald determined apparent constants, based on molarities rather than on activities, and at an ionic strength only about one-fifth that of sea water. We decided upon a study of the effects of addition of NaCl , MgCl_2 , and mixtures of the two salts on the activity coefficients of HCO_3^- and CO_3^{--} in aqueous solution. Our experiments were such that it became possible to calculate thermodynamic dissociation constants (based on activities) for the carbonate complexes, and to test the validity of the constants over a range of ionic strengths, up to and including that of sea water. All work was done at 25°C, and one atmosphere total pressure.

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TERMINOLOGY

The following definitions of terms will be useful in following the text.

a_i = activity of the i th species, that is, thermodynamic concentration of a given ion, e. g., $a_{\text{CO}_3^{--}}$.

- $m_{1(T)}$ = total concentration of a dissolved constituent (mols per 1000g H_2O) as determined analytically, e. g., $m_{CO_3^{--}(T)}$ equals carbonate ion per 1000g H_2O , as determined by titration with a standard acid. Total concentration also is specified by addition of measured amounts of an analytical reagent to the test solution.
- m_1 = calculated concentration of a dissolved species (mols per 1000g H_2O). It generally represents "free" or "uncomplexed" species.
- $m_{1(complexed)}$ = difference between $m_{1(T)}$ and m_1 .
- $\gamma_{1(T)}$ = total or apparent activity coefficient = ratio of activity of a dissolved constituent to its total concentration, $(a_1/m_{1(T)})$.
- γ_1 = activity coefficient = ratio of activity of a dissolved species to the concentration of "uncomplexed" species, (a_1/m_1) .
- K' = apparent "constants" calculated using molality ratios and products.
- K = equilibrium constant, calculated using activities, e. g.,
- $$\frac{a_{H^+} a_{CO_3^{--}}}{a_{HCO_3^-}} = K_{HCO_3^-}$$
- $m_{MgCO_3^0}$ = concentration of uncharged magnesium-carbonate ion pairs in solution. The exponent ^{0} is used to distinguish the dissolved species from the solid.
- μ = ionic strength = $\frac{1}{2} \sum_i m_{i(T)} z_i^2$, where z_i is the charge on the ionic constituent.

EXPERIMENTAL WORK

Reagent Grade chemicals were used throughout the experiments. CO_2 and N_2 were obtained from commercial tanks, and were passed through water before being passed through distilled water solutions to avoid undue evaporation of the solutions. The experiments were run in flat-bottomed cylindrical pyrex containers capable of holding about 500 ml of water. Covers for the containers were made of quarter-inch plastic plate with stoppered holes. Communication with the solution was achieved by mounting a set of pH-measuring electrodes in rubber stoppers and inserting them through the holes in the cover. The pH measurements were made with a Beckman-type "E" glass electrode designed for use in solutions of high pH, and a "saturated" calomel reference electrode. A resistance thermometer was used for temperature compensation and a platinum electrode for solution grounding. Leads from the electrodes were connected to an amplifier and an automatic recorder, the pH of the solution was recorded every 18 seconds. The apparatus was well balanced for measurements of pH to within 0.01 pH units; we estimate the accuracy of individual measurements as about ± 0.02 pH units.

PROCEDURE

After the electrodes has been standardized on both pH 4 and pH 7 buffers to within 0.01 pH units, 400 ml (399g) of distilled water was measured into

the container. To prepare a solution of NaHCO_3 , a weighed amount of Na_2CO_3 was added, and CO_2 passed through the solution. When the pH became constant, weighed amounts of solid NaCl or measured amounts of MgCl_2 solution were added. Readings were made at 25°C after the pH had remained constant for several minutes.

To prepare a solution of CO_3^{--} and HCO_3^- , the water was swept with purified N_2 to a pH of 7.0 before weighed Na_2CO_3 was added. Then the solution was titrated with standard HCl to the desired ratio of CO_3^{--} to HCO_3^- , $(m_{\text{CO}_3^{--}(\text{T})}/m_{\text{HCO}_3^-(\text{T})})$. Then, as above, NaCl and/or MgCl_2 were added. (In these solutions, P_{CO_2} is very low, and loss of CO_2 is found, by titration, to be negligible).

Each experiment took about an hour to complete; the temperature was controlled at $25^\circ \pm 0.5^\circ\text{C}$ by setting the solution container in a small water bath. Solutions were stirred by means of magnetic bars inside the containers.

RESULTS

The results of the experiments are given in table I.

TABLE I
Results of experimental work

a. Change of pH of NaHCO ₃ solution with added NaCl.				
P _{CO₂}	1	Date	6/1/59	
Wt. Na ₂ CO ₃	2.1413g	Salt	NaCl	
Vol. H ₂ O	400ml.	Temperature	25°C	
Equation	$\gamma_{\text{HCO}_3^-(\text{T})} = \frac{10^{-\text{pH}} a_{\text{H}_2\text{O}}}{a_{\text{H}^+} m_{\text{HCO}_3^-(\text{T})}}$			
gNaCl	μ	pH	pa _{H₂O}	$\gamma_{\text{HCO}_3^-(\text{T})}$
0	0.101	6.695	0.001	0.739
5.845	0.351	6.55	0.0055	0.524
11.690	0.60	6.50	0.0095	0.456
17.535	0.85	6.46	0.014	0.418
23.38	1.10	6.43	0.0175	0.387
35.07	1.60	6.38	0.025	0.339
46.76	2.10	6.34	0.032	0.304
70.14	3.10	6.29	0.050	0.260
93.52	4.10	6.26	0.078	0.230
116.90	5.10	6.21	0.102	0.192

b. Change of pH of NaHCO_3 solution with added MgCl_2 solution.

P_{CO_2}	1	Date	6/23/59
Wt. Na_2CO_3	0.2685g	Salt	MgCl_2
Vol. H_2O	400ml.	Temperature	25°C

$$\text{Equation} \quad \gamma_{\text{HCO}_3^-(T)} = \frac{10^{-\tau_{\text{HCO}_3^-}} a_{\text{H}_2\text{O}}}{a_{\text{H}^+} m_{\text{HCO}_3^-(T)}}$$

mls H_2O	g MgCl_2	μ	pH	$p_{\text{a}_{\text{H}_2\text{O}}}$	$\gamma_{\text{HCO}_3^-(T)}$
400.0	0	0.013	5.88	—	0.905
401.9	0.373	0.042	5.79	—	0.745
403.8	0.745	0.071	5.74	—	0.668
405.8	1.119	0.099	5.705	0.001	0.616
407.7	1.492	0.128	5.68	0.002	0.585
409.6	1.863	0.156	5.66	0.0025	0.560
414.3	2.794	0.224	5.62	0.0035	0.515
419.0	3.725	0.291	5.59	0.004	0.485
423.7	4.656	0.357	5.56	0.0055	0.456
428.4	5.59	0.422	5.53	0.0065	0.430
433.1	6.52	0.485	5.51	0.007	0.415
437.8	7.45	0.547	5.495	0.0085	0.404
442.5	8.38	0.608	5.49	0.0095	0.393
447.2	9.31	0.668	5.46	0.010	0.397

c. Change of pH of NaHCO_3 solution with added NaCl and MgCl_2 solution.

P_{CO_2}	1	Date	6/26/59
Wt. Na_2CO_3	0.2638g	Salt	NaCl and MgCl_2
Vol. H_2O	400ml	Temperature	25°C

$$\text{Equation} \quad \gamma_{\text{HCO}_3^-(T)} = \frac{10^{-\tau_{\text{HCO}_3^-}} a_{\text{H}_2\text{O}}}{a_{\text{H}^+} m_{\text{HCO}_3^-(T)}}$$

mls H_2O	g MgCl_2	g NaCl	pH	$p_{\text{a}_{\text{H}_2\text{O}}}$	μ	$\gamma_{\text{HCO}_3^-(T)}$
400.0	0	0	5.92	—	0.012	—
401.9	0.373	2.22	5.74	0.002	0.136	0.666
403.8	0.745	4.44	5.67	0.004	0.259	0.569
405.7	1.119	6.66	5.62	0.006	0.380	0.506
407.6	1.492	8.88	5.60	0.0075	0.501	0.485
409.5	1.863	11.10	5.575	0.009	0.621	0.458
414.1	2.794	16.65	5.50	0.014	0.921	0.384

d. Change of pH of Na_2CO_3 - NaHCO_3 solution with added NaCl .

P _{CO₂}	—	Date	6/2/59
Wt. Na ₂ CO ₃	2.0390g	Salt	NaCl
Vol. H ₂ O	400ml	Temperature	25°C
HCl 5.50 mls.,	0.9035m	$m_{\text{HCO}_3^-} / m_{\text{CO}_3^{--}} = 10^{-0.49}$	
Equation	$\gamma_{\text{CO}_3^{--}} = \frac{10^{-10.83} \gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-}}{a_{\text{H}^+} m_{\text{CO}_3^{--}}}$		

gNaCl	pH	μ	$\gamma_{\text{CO}_3^{--}}$	$-\log \frac{\gamma_{\text{CO}_3^{--}}}{\gamma_{\text{HCO}_3^-}}$
0.01	10.33	0.112	0.250	0.457
5.85	10.07	0.362	0.100	0.717
11.69	9.96	0.612	0.068	0.827
17.54	9.86	0.862	0.049	0.927
23.38	9.79	1.112	0.039	0.997
35.07	9.65	1.612	0.025	1.137
46.76	9.56	2.112	0.018	1.227
71.14	9.42	3.112	0.011	1.367
93.52	9.32	4.112	0.008	1.467
116.90	9.24	5.112	0.006	1.547

e. Change of pH of NaHCO_3 - Na_2CO_3 solution with added NaCl .

P _{CO₂}	—	Date	6/4/59	
Wt. Na ₂ CO ₃	2.3413g	Salt	NaCl	
Vol. H ₂ O	400ml	Temperature	25°C	
HCl 15.00 mls.,	0.9035m	$m_{\text{HCO}_3^{-(\text{cr})}} / m_{\text{CO}_3^{--(\text{cr})}} = 10^{+0.199}$		
Equation	$\gamma_{\text{CO}_3^{--(\text{cr})}} = \frac{10^{-10.83} \gamma_{\text{HCO}_3^{-(\text{cr})}} m_{\text{HCO}_3^{-(\text{cr})}}}{a_{\text{H}^+} m_{\text{CO}_3^{--(\text{cr})}}}$			
gNaCl	pH	μ	$\gamma_{\text{CO}_3^{--(\text{cr})}}$	$-\log \frac{\gamma_{\text{CO}_3^{--(\text{cr})}}}{\gamma_{\text{HCO}_3^{-(\text{cr})}}}$
0.03	9.66	0.125	0.233	0.475
5.85	9.42	0.375	0.100	0.715
11.69	9.29	0.625	0.065	0.845
17.54	9.20	0.875	0.048	0.935
23.38	9.11	1.125	0.036	1.025
35.07	9.00	1.625	0.025	1.135
46.76	8.90	2.125	0.018	1.235
67.14	8.79	2.945	0.012	1.345
93.52	8.65	4.125	0.007	1.485
116.90	8.57	5.125	0.005	1.565

f. Change of pH of NaHCO_3 - Na_2CO_3 solution with added MgCl_2 solution.

P _{CO₂}	—	Date	6/22/59		
Wt. Na ₂ CO ₃	0.9813g	Salt	MgCl ₂		
Vol. H ₂ O	400ml	Temperature	25°C		
HCl 5.12 mls	0.9035m	$m_{\text{HCO}_3^{-(\text{cr})}} =$	$m_{\text{CO}_3^{--(\text{cr})}}$		
Equation	$\gamma_{\text{CO}_3^{--(\text{cr})}} = \frac{10^{-10.25} \gamma_{\text{HCO}_3^{-(\text{cr})}} m_{\text{HCO}_3^{-(\text{cr})}}}{a_{\text{H}^+} m_{\text{CO}_3^{--(\text{cr})}}}$				
mls H ₂ O	g MgCl ₂	pH	μ	$\gamma_{\text{CO}_3^{--(\text{cr})}}$	$-\log \frac{\gamma_{\text{CO}_3^{--(\text{cr})}}}{\gamma_{\text{HCO}_3^{-(\text{cr})}}}$
405.1	0	9.80	0.057		
407.0	0.373	9.56	0.086	0.1085	0.77
408.9	0.745	9.37	0.114	0.066	0.96
410.8	1.119	9.22	0.142	0.044	1.11
412.7	1.492	9.11	0.170	0.033	1.22
414.5	1.863	9.03	0.198	0.027	1.30
416.4	2.236	8.97	0.224	0.022	1.36
418.3	2.608	8.91	0.252	0.019	1.42
420.2	2.981	8.87	0.279	0.017	1.46
422.1	3.354	8.83	0.304	0.015	1.50
423.9	3.725	8.80	0.331	0.0138	1.53
425.8	4.096	8.75	0.357	0.0119	1.58
427.7	4.471	8.71	0.383	0.0109	1.62
429.6	4.843	8.67	0.408	0.0096	1.66
431.5	5.216	8.64	0.434	0.0088	1.69
433.3	5.588	8.63	0.459	0.0085	1.70

g. Change of pH of NaHCO_3 - Na_2CO_3 solution with added NaCl and MgCl_2 solution.

P _{CO₂}	0	Date	6/18/59			
Wt. Na ₂ CO ₃	1.0423g	Salt	NaCl and MgCl ₂			
Vol. H ₂ O	400 mls	Temperature	25°C.			
HCl 5.44 mls.	0.9035m	m _{HCO₃⁻(cr)} =	m _{CO₃⁻⁻(cr)}			
Equation	$\gamma_{\text{CO}_3^{--}(\text{cr})} = \frac{10^{-10.25} \gamma_{\text{HCO}_3^{-}(\text{cr})} m_{\text{HCO}_3^{-}(\text{cr})}}{a_{\text{H}^+} m_{\text{CO}_3^{--}(\text{cr})}}$					
mls H ₂ O	g MgCl ₂	g NaCl	μ	pH	γ _{CO₃⁻⁻(cr)}	-log $\frac{\gamma_{\text{CO}_3^{--}(\text{cr})}}{\gamma_{\text{HCO}_3^{-}(\text{cr})}}$
405.4	0	0.01	0.061	9.92		
407.3	0.373	2.25	0.186	9.55	0.102	0.78
409.2	0.745	4.44	0.305	9.38	0.061	0.95
411.1	1.119	6.66	0.423	9.25	0.041	1.08
413.0	1.492	8.88	0.542	9.14	0.029	1.19
414.9	1.863	11.10	0.665	9.06	0.022	1.27
419.6	2.794	16.65	0.952	8.91	0.014	1.42

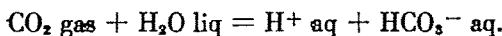
DISCUSSION

From the data in table 1, it is clear that the pH values of solutions containing HCO_3^- and H_2CO_3 , or HCO_3^- and CO_3^{--} , are affected differently by addition of NaCl , MgCl_2 , or mixtures of the two salts, even if they are compared at the same ionic strength (μ).

A. HCO_3^- solutions.—Considering first the effects of neutral salt additions to NaHCO_3 solutions, we found that the most satisfactory representation was in terms of the ratio of the activity of HCO_3^- to its total concentration (or analytically determined concentration). The ratio of $a_{\text{HCO}_3^-}$ to total bicarbonate ($m_{\text{HCO}_3^- \text{ (T)}}$) is designated the total activity coefficient:

$$\frac{a_{\text{HCO}_3^-}}{m_{\text{HCO}_3^- \text{ (T)}}} = \gamma_{\text{HCO}_3^- \text{ (T)}}$$

This ratio can be obtained from the reaction



At equilibrium we can calculate, from free energy values in Latimer (1952),

$$\frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{a_{\text{CO}_2 \text{ gas}} a_{\text{H}_2\text{O}}} = K_{\text{CO}_2} = 10^{-7.82} \quad (1)$$

Rewriting in terms of activity coefficients and analytical molalities of HCO_3^-

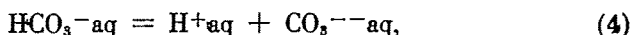
$$\frac{a_{\text{H}^+} \gamma_{\text{HCO}_3^- \text{ (T)}} m_{\text{HCO}_3^- \text{ (T)}}}{a_{\text{CO}_2} a_{\text{H}_2\text{O}}} = 10^{-7.82} \quad (2)$$

Rearranging

$$\gamma_{\text{HCO}_3^- \text{ (T)}} = \frac{10^{-7.82} a_{\text{CO}_2} a_{\text{H}_2\text{O}}}{a_{\text{H}^+} m_{\text{HCO}_3^- \text{ (T)}}} \quad (3)$$

The activity of CO_2 is fixed at unity by maintaining one atmosphere CO_2 pressure¹; the activity of H_2O in salt solutions is available (Int. Crit. Tables, p. 370), and the activity of H^+ is measured directly by a glass-calomel electrode pair. $m_{\text{HCO}_3^- \text{ (T)}}$ is known from the amount of NaHCO_3 in the solution at the start of the run, and moreover can be measured directly at the end of a run by titration with a standard acid.

B. $\text{HCO}_3^- - \text{CO}_3^{--}$ solutions.—In solutions containing both CO_3^{--} and HCO_3^- (table 1, d,e,f,g), it is possible to obtain ratios of $\gamma_{\text{CO}_3^{--} \text{ (T)}}$ to $\gamma_{\text{HCO}_3^- \text{ (T)}}$ as follows. From the reaction,



¹ Actually, $P_{\text{CO}_2} + P_{\text{H}_2\text{O}} = 1$, but the correction for the vapor pressure of H_2O is not significant in our calculations. We also make the approximation that partial pressure of CO_2 = fugacity of CO_2 = activity of CO_2 .

at equilibrium, from free energy data in Latimer (1952), we can calculate

$$\frac{a_{H^+} a_{CO_3^{--}}}{a_{HCO_3^-}} = K_{HCO_3^-} = 10^{-10.33} \quad (5)$$

Rewriting in terms of total activity coefficients and analytical molalities of HCO_3^- and CO_3^{--} ,

$$\frac{a_{H^+} \gamma_{CO_3^{--}(\tau)} m_{CO_3^{--}(\tau)}}{\gamma_{HCO_3^-(\tau)} m_{HCO_3^-(\tau)}} = 10^{-10.33} \quad (6)$$

Rearranging,

$$\frac{\gamma_{CO_3^{--}(\tau)}}{\gamma_{HCO_3^-(\tau)}} = \frac{10^{-10.33} m_{HCO_3^-(\tau)}}{a_{H^+} m_{CO_3^{--}(\tau)}} \quad (7)$$

Under the experimental conditions pH is measured, as before, by the glass-calomel electrode pair; $m_{HCO_3^-(\tau)}$ and $m_{CO_3^{--}(\tau)}$ are known from the titration of a solution of weighed Na_2CO_3 with standard HCl. Thus the experiments provide a ratio of the total activity coefficients.

Figure 1 is a plot of $\gamma_{HCO_3^-(\tau)}$ versus ionic strength (μ) for various experimental runs. Also shown are values for $KHCO_3$ and $NaHCO_3$ from Walker, Bray, and Johnston (1927), and as calculated from the Debye-Hückel theory (Klotz, 1950, p. 329). This plot shows that: (1) $\gamma_{HCO_3^-(\tau)}$ is a maximum in

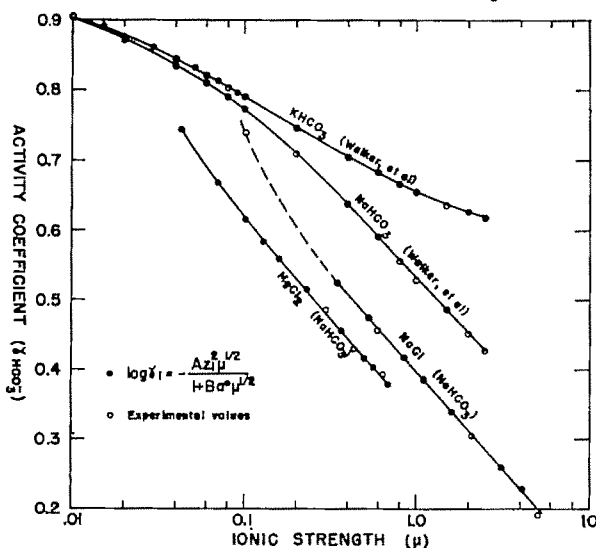


Fig. 1. $\gamma_{HCO_3^-(\tau)}$ versus ionic strength for various solutions.

$KHCO_3$ solutions, and compares closely to values calculated entirely on the basis of expected ionic interaction (Debye-Huckel). (2) $\gamma_{HCO_3^-(\tau)}$ is markedly lower in NaCl solutions. (3) $\gamma_{HCO_3^-(\tau)}$ is a minimum in $MgCl_2$ solutions.

Our conclusion is that $KHCO_3$ solutions provide a fair measure of

the values of $\gamma_{\text{HCO}_3^-(\text{cr})}$ that occur in the absence of any complexing, and that HCO_3^- is mildly complexed by both NaCl and MgCl_2 solutions. The degree of complexing is not great, as shown by the relatively small differences in $\gamma_{\text{HCO}_3^-}$ from salt to salt. We attempted to test various models, such as NaHCO_3^0 , $\text{Na}(\text{HCO}_3)_2^-$, and $\text{Na}(\text{HCO}_3)_3^{--}$, but found that the errors involved in testing the models are of the same order of magnitude as the degree of association involved in the complex. Greenwald (1941) has obtained an apparent dissociation constant of 1.7×10^{-1} for a MgHCO_3^+ complex at a μ of 0.15. This complex and constant fit our data fairly well. However, we found that a $\text{Mg}(\text{HCO}_3)_2^-$ complex can also be used to interpret our data. Our conclusion, therefore, is that complexing does occur, but that direct comparison of $\gamma_{\text{HCO}_3^-(\text{cr})}$ values for the various salt additions is the most satisfactory method for assessing its importance. MgCl_2 , NaCl , and mixtures of MgCl_2 and NaCl all give $\gamma_{\text{HCO}_3^-(\text{cr})}$ values in the general range of sea water (Sverdrup, 1942, p. 205) at equivalent μ .

Figure 2 shows plots of the ratio of $-\log \frac{\gamma_{\text{HCO}_3^-(\text{cr})}}{\gamma_{\text{CO}_3^{--}(\text{cr})}}$ as determined from our experiments, in NaCl solution, in MgCl_2 solution, and in a solution having a constant mol ratio of one MgCl_2 to ten NaCl — approximating the ratio found in sea water.

Also included in the figure is a curve for $\text{K}_2\text{CO}_3 - \text{KHCO}_3$ solutions taken from Walker, Bray, and Johnston (1927).

For purposes of comparison with the experimentally determined ratios, that calculated for sea water from the data in Sverdrup (1942) is shown. The

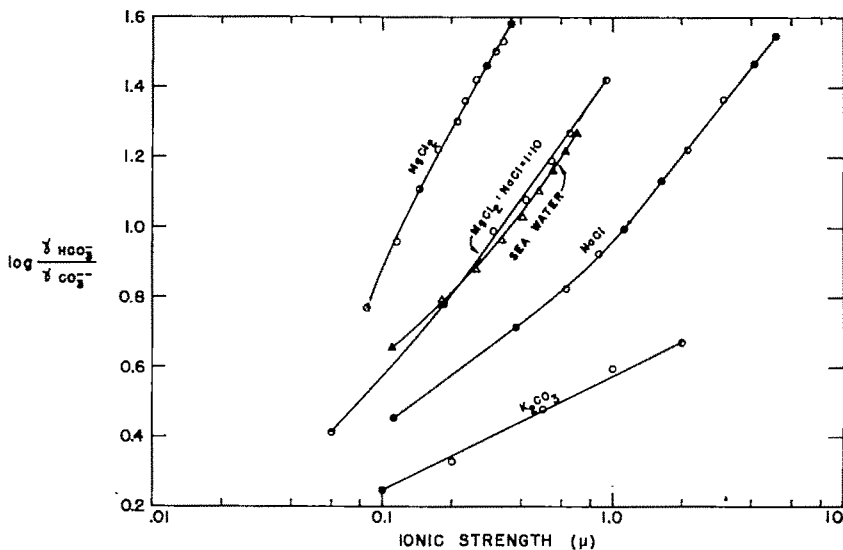


Fig. 2. $\log \frac{\gamma_{\text{CO}_3^{--}(\text{cr})}}{\gamma_{\text{HCO}_3^-(\text{cr})}}$ versus ionic strength for various solutions.

calculation uses an empirical equation relating the apparent second dissociation constant of H_2CO_3 (K'_2) and the chlorinity of sea water at various ionic strengths.

Figure 3 shows values for $\gamma_{\text{CO}_3^{--(\text{m})}}$, obtained by substituting values of $\gamma_{\text{HCO}_3^{-(\text{m})}}$ from data obtained in HCO_3^- solutions (fig. 1) into the $\gamma_{\text{HCO}_3^{-(\text{m})}}/\gamma_{\text{CO}_3^{--(\text{m})}}$ ratios. In the same figure values are shown as calculated by Debye-Hückel theory, as well as from mean activity coefficients of K_2CO_3 and KCl (Walker, Bray, and Johnston, 1927), and for sea water (Sverdrup, 1942, p. 200-205).

The general relations are similar to those for $\gamma_{\text{HCO}_3^{-(\text{m})}}$, but the differential salt effects are much more pronounced. To summarize the relations: (1) The approximate equivalence of $\gamma_{\text{CO}_3^{--}}$ as determined theoretically (Debye-Hückel) and in K_2CO_3 solutions indicates that in solutions containing only potassium salts there is little ion association, and that $\gamma_{\text{CO}_3^{--(\text{m})}}$ is approximately that expected simply from the electrical effects of the ions present, or in our terminology, that $\gamma_{\text{CO}_3^{--(\text{m})}\text{K}_2\text{CO}_3} = \gamma_{\text{CO}_3^{--}}$. (2) The marked decrease of $\gamma_{\text{CO}_3^{--(\text{m})}}$ in NaCl solutions over that in KCl solutions is strong evidence of the presence of complex ions. (3) The further decrease of $\gamma_{\text{CO}_3^{--(\text{m})}}$ in MgCl_2 solutions is indicative of even greater complex formation in the presence of Mg^{++} . (4) The near identity of $\gamma_{\text{CO}_3^{--(\text{m})}}$ values in $\text{MgCl}_2\text{-NaCl}$ mixtures resembling sea water, and observed values in sea water, shows that the primary control of $\gamma_{\text{CO}_3^{--(\text{m})}}$ in sea water is the NaCl-MgCl_2 ratio, and the low values of $\gamma_{\text{CO}_3^{--(\text{m})}}$ are not attributable to organic complexing, or to complexing by other inorganic ions. (5) Because $\gamma_{\text{CO}_3^{--(\text{m})}}$ is a critical factor in the solubility

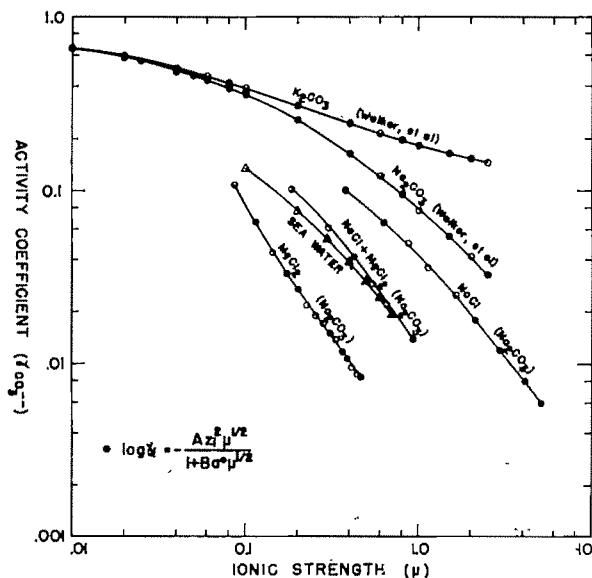


Fig. 3. $\gamma_{\text{CO}_3^{--(\text{m})}}$ versus ionic strength for various solutions.

of carbonate minerals, it is clear that the NaCl-MgCl_2 ratio in sea water and in other salt solutions is of utmost importance in controlling the absolute solubility of calcite, aragonite, dolomite, and other carbonates deposited under marine or subsurface brine conditions.

The MgCO_3^0 complex.—Although it was not possible to establish the nature of the complexes of Na^+ and Mg^{++} with HCO_3^- , the much greater deviation of $\gamma_{\text{CO}_3^{--}(\text{M})}$ values from those expected simply from general ionic interaction permits determination of the specific nature of the complexes of CO_3^{--} with Mg^{++} and Na^+ . We tested various possibilities, and found that the best fit of the data for Mg results from the assumption that the only complex of Mg in solution is the ion pair MgCO_3^0 .

In the calculation we have made the fundamental assumption that $\gamma_{\text{CO}_3^{--}(\text{M})}$ in K_2CO_3 solutions is an accurate measure of the difference between activity and concentration, i.e., the difference to be expected simply from electrical interaction of the ions without important ion association. Therefore, in our calculations, we assume that $\gamma_{\text{CO}_3^{--}(\text{M})\text{K}_2\text{CO}_3} = \gamma_{\text{CO}_3^{--}}$. Thus the activity of CO_3^{--} in a MgCl_2 solution is related to the molality of complexed CO_3^{--} by the relation

$$\frac{a_{\text{CO}_3^{--}(\text{MgCl}_2)}}{\gamma_{\text{CO}_3^{--}(\text{M})\text{K}_2\text{CO}_3}} = \frac{a_{\text{CO}_3^{--}(\text{MgCl}_2)}}{\gamma_{\text{CO}_3^{--}}} = m_{\text{CO}_3^{--}(\text{uncomplexed})} \quad (8)$$

Then the concentration of complexed CO_3^{--} is given by

$$m_{\text{CO}_3^{--}(\text{complexed})} = m_{\text{CO}_3^{--}(\text{M})} - m_{\text{CO}_3^{--}(\text{uncomplexed})} \quad (9)$$

The activity coefficient of Mg^{++} , in the absence of complexes, can be derived by assuming that the mean activity coefficient of MgCl_2 is the geometric mean of the activity coefficient of Mg^{++} and that of Cl^- , and furthermore that the mean activity coefficient of KCl is equivalent to the activity coefficient of Cl^- . These assumptions have been used widely in the past (cf. Lewis and Randall, 1923, p. 381). Then

$$\gamma_{\text{Mg}^{++}} = \frac{\gamma^{\pm \text{MgCl}_2}}{\gamma^{\pm \text{KCl}}}$$

Values of $\gamma_{\text{Mg}^{++}}$ derived in this way from data in Latimer (1952, p. 355) are shown in figure 4. For ionic strengths of 0.1 and less, the points on the curve are calculated from the Debye-Hückel equation

$$\log \gamma_i = - \frac{Az_i^2 \mu^{1/2}}{1 + B a^0 \mu^{1/2}}$$

Values of γ_{Na^+} and $\gamma_{\text{Ca}^{++}}$, obtained in a similar manner from data in Latimer (1952, p. 354-356), and from the Debye-Hückel equation, are shown in the same figure.

From the reaction,



we see that the molality of Mg^{++} is equal to the total concentration of Mg added, less that tied up in the MgCO_3^0 complex:

$$m_{\text{Mg}^{++}(\text{uncomplexed})} = m_{\text{Mg}^{++}(\text{M})} - m_{\text{MgCO}_3^0} \quad (11)$$

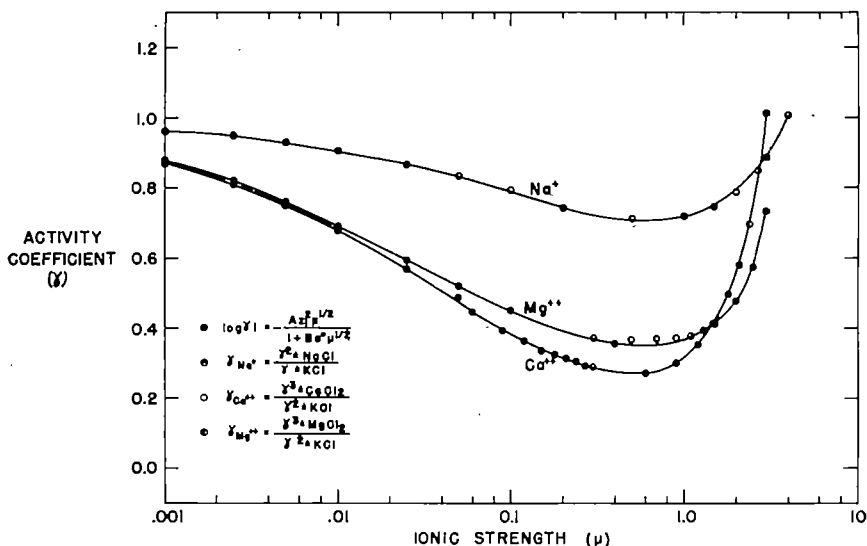


Fig. 4. Activity coefficients for Na^+ , Mg^{++} , and Ca^{++} versus ionic strength, calculated from published data.

But the molality of complexed Mg^{++} is equal to the molality of complexed carbonate. The equilibrium constant, K dissociation, for reaction #10 is

$$\frac{a_{\text{Mg}^{++}} a_{\text{CO}_3^{--}}}{a_{\text{MgCO}_3^0}} = K_{\text{MgCO}_3^0} \quad (12)$$

Table 2 gives sequentially the values necessary to test $K_{\text{MgCO}_3^0}$.

The data are taken from the experiment (table 1, f) in which a solution having initial equal molalities of CO_3^{--} and HCO_3^- was titrated with MgCl_2 solution, and the change in pH with change in $m_{\text{Mg}^{++}(\text{t})}$ was noted. The data are arranged in columns as follows:

1. Ionic strength, (μ). This is calculated as one-half the sum of $m_{\text{Na}^+(\text{t})} + m_{\text{Cl}^-(\text{t})} + m_{\text{HCO}_3^-(\text{t})} + 4m_{\text{Mg}^{++}(\text{t})} + 4m_{\text{CO}_3^{--}(\text{t})}$. The effect of complexes on μ is not considered.

2. $a_{\text{CO}_3^{--}}$, calculated from equation (6), $m_{\text{HCO}_3^-(\text{t})}$, $\gamma_{\text{HCO}_3^-(\text{t})(\text{MgCl}_2)}$, and pH.

3. $\gamma_{\text{CO}_3^{--}(\text{K}_2\text{CO}_3)}$.

4. $m_{\text{CO}_3^{--}(\text{uncomplexed})}$, (equation (8)).

5. $m_{\text{MgCO}_3^0}$ (equation (9)), equal to $m_{\text{CO}_3^{--}(\text{complexed})}$.

6. $\gamma_{\text{MgCO}_3^0}$, assuming that the activity coefficient of a molecular complex is the same as that of H_2CO_3 (Harned and Owen, 1958, p. 531-540).

Values for $\gamma_{\text{H}_2\text{CO}_3}$ are calculated from the data of Markham and Kobe (1941).

TABLE 2

The calculation of the constant $K = \frac{a_{M^{++}} a_{CO_3^{--}}}{a_{MCO_3^0}}$

1	2	3	4	5	6
μ	$a_{CO_3^{--}}$	$\gamma_{CO_3^{--}}$ (K_2CO_3)	$m_{CO_3^{--}}$ uncomplexed	$m_{MCO_3^0}$ or $m_{CO_3^{--}}$ complexed	$\gamma_{MCO_3^0}$
$\times 10^3$	$\times 10^4$	$\times 10$	$\times 10^4$	$\times 10^3$	
5.7	23.6	4.60	51.4	—	—
8.6	12.31	4.07	30.2	8.34	1.020
11.4	7.44	3.73	19.9	9.33	1.025
14.2	5.01	3.43	14.6	9.78	1.030
17.0	3.71	3.21	11.5	10.05	1.035
19.8	2.97	3.08	9.6	10.20	1.040
22.4	2.50	2.95	8.5	10.26	1.045
25.2	2.10	2.85	7.4	10.33	1.050
27.9	1.863	2.75	6.8	10.32	1.055
30.4	1.652	2.68	6.2	10.33	1.060
33.1	1.485	2.60	5.7	10.34	1.065
35.7	1.299	2.53	5.2	10.33	1.070
38.3	1.160	2.48	4.7	10.34	1.075
40.8	1.037	2.42	4.3	10.35	1.080
43.4	0.946	2.38	4.0	10.31	1.085
45.9	0.910	2.34	3.9	10.29	1.090
7	8	9	10	11	12
$a_{MCO_3^0}$	$m_{M^{++}}(T)$	$m_{M^{++}}$ uncomplexed	$\gamma_{M^{++}}$	$a_{M^{++}}$	$\frac{a_{M^{++}} a_{CO_3^{--}}}{a_{MCO_3^0}}$
$\times 10^3$	$\times 10^2$	$\times 10^2$	$\times 10$	$\times 10^3$	$\times 10^4$
—	0	—	—	—	—
8.71	0.970	0.136	4.73	0.644	0.93
9.55	1.932	0.999	4.34	4.32	3.36
10.08	2.860	1.902	4.15	7.90	3.93
10.41	3.830	2.825	4.01	11.76	4.20
10.60	4.77	3.750	3.92	14.70	4.11
10.70	5.69	4.664	3.85	17.98	4.10
10.85	6.62	5.587	3.80	21.20	4.11
10.90	7.52	6.488	3.76	24.41	4.18
10.96	8.42	7.387	3.73	27.59	4.15
11.00	9.34	8.306	3.69	30.62	4.19
11.06	10.17	9.137	3.67	33.50	3.94
11.10	11.09	10.056	3.65	36.70	3.83
11.16	11.97	10.935	3.63	39.70	3.68
11.19	12.81	11.779	3.62	42.60	3.61
11.23	13.67	12.641	3.62	45.75	3.70

7. $a_{\text{MgCO}_3^0}$, the product of values in columns 5 and 6, $\gamma_{\text{MgCO}_3^0}$ times $m_{\text{MgCO}_3^0}$.
8. $m_{\text{Mg}^{++}(\text{C})}$, added as MgCl_2 .
9. $m_{\text{Mg}^{++}}$, i. e., that remaining after subtraction of the Mg^{++} tied up as MgCO_3^0 (equation (11)).
10. $\gamma_{\text{Mg}^{++}}$, derived from $\gamma \pm \text{MgCl}_2$ and $\gamma \pm \text{KCl}$ (fig. 4).
11. $a_{\text{Mg}^{++}}$, the product of values in columns 9 and 10, $m_{\text{Mg}^{++}}$ times $\gamma_{\text{Mg}^{++}}$.
12. $\frac{a_{\text{Mg}^{++}} a_{\text{CO}_3^{--}}}{a_{\text{MgCO}_3^0}}$, using values from columns 2, 11, and 7.

Figure 5 shows values of $\frac{a_{\text{Mg}^{++}} a_{\text{CO}_3^{--}}}{a_{\text{MgCO}_3^0}}$ from column 12, table 2, plotted against ionic strength. Neglecting the first two points, the values range from 3.6 to 4.2 times 10^{-4} and show no trend with increase in μ . The best value for $K_{\text{MgCO}_3^0}$ is 4.0 ± 0.2 times 10^{-4} , or $10^{-3.4}$. The values in table 2 show that most of the CO_3^{--} is tied up as complex, so that the concentration of MgCO_3^0 is essentially constant, whereas the concentrations of Mg^{++} and CO_3^{--} show a reciprocal relation.

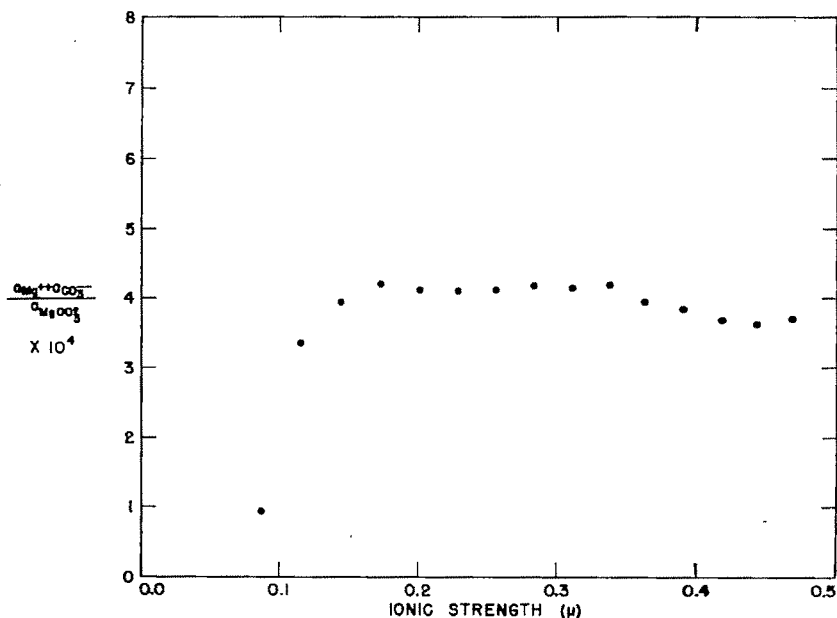


Fig. 5. $\frac{a_{\text{Mg}^{++}} a_{\text{CO}_3^{--}}}{a_{\text{MgCO}_3^0}}$ versus ionic strength.

The NaCO₃⁻ complex.—In NaCl solution the values of $\gamma_{\text{CO}_3^{--}}$ are not as low as in MgCl₂ solution, but the deviation from values expected in the absence of complexes is still marked. Table 3 shows a series of values derived in essentially the same manner as was used in assessing the nature of the MgCO₃⁰ complex. As in that instance, a casual inspection of the values of m_{Na^+} and $m_{\text{CO}_3^{--}}$, or a_{Na^+} and $a_{\text{CO}_3^{--}}$ indicate a reciprocal relationship. Therefore a complex analogous to the MgCO₃⁰ ion pair is indicated thus:

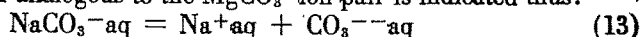


TABLE 3

The calculation of the constant $K = \frac{a_{\text{Na}^+} a_{\text{CO}_3^{--}}}{a_{\text{NaCO}_3^-}}$

1	2	3	4	5	6
μ	$a_{\text{CO}_3^{--}}$	$\gamma_{\text{CO}_3^{--}}$ (K ₂ CO ₃)	$m_{\text{CO}_3^{--}}$ uncomplexed	$m_{\text{NaCO}_3^-}$ or $m_{\text{CO}_3^{--}}$ complexed	$\gamma_{\text{NaCO}_3^-}$ ($\gamma_{\text{HCO}_3^-}$)
	$\times 10^4$	$\times 10$	$\times 10^3$	$\times 10^3$	$\times 10$
0.112	65.0	4.88	13.32	1.242	7.85
0.362	26.4	2.83	9.33	1.747	7.16
0.612	17.7	2.10	8.41	1.839	6.86
0.862	12.9	1.79	7.17	1.963	6.68
1.112	10.1	1.61	6.24	2.056	6.54
1.612	6.36	1.41	4.55	2.225	6.40
2.112	4.66	1.30	3.57	2.323	6.26
3.112	2.90	(1.19)	2.43	2.437	6.11
4.112	2.03	(1.13)	1.97	2.483	6.00
5.112	1.56	(1.10)	1.41	2.539	5.90
7	8	9	10	11	12
$a_{\text{NaCO}_3^-}$	m_{Na^+} (C)	m_{Na^+} uncomplexed	γ_{Na^+}	a_{Na^+}	$a_{\text{Na}^+} a_{\text{CO}_3^{--}}$ $a_{\text{NaCO}_3^-}$
$\times 10^3$					$\times 10^3$
0.976	0.096	0.084	0.777	0.065	4.34
1.250	0.346	0.329	0.722	0.237	5.02
1.261	0.596	0.578	0.715	0.413	5.80
1.312	0.846	0.827	0.716	0.592	5.80
1.343	1.096	1.076	0.726	0.781	5.85
1.422	1.596	1.574	0.755	1.189	5.83
1.460	2.096	2.073	0.792	1.640	5.25
1.490	3.096	3.072	0.910	2.795	5.44
1.490	4.096	4.071	1.080	4.400	5.99
1.500	5.096	5.071	1.380	7.000	7.29

The equilibrium constant (figure 6) is:

$$\frac{a_{\text{Na}^+} a_{\text{CO}_3^{--}}}{a_{\text{NaCO}_3^-}} = K = 0.054 \pm 0.005 \quad (14)$$

The values of K shown in the last column of table 3 and in figure 6 are satisfactory within the limits of the various assumptions that must be made (e.g., that $\gamma_{\text{NaCO}_3^-} = \gamma_{\text{HCO}_3^-}$).

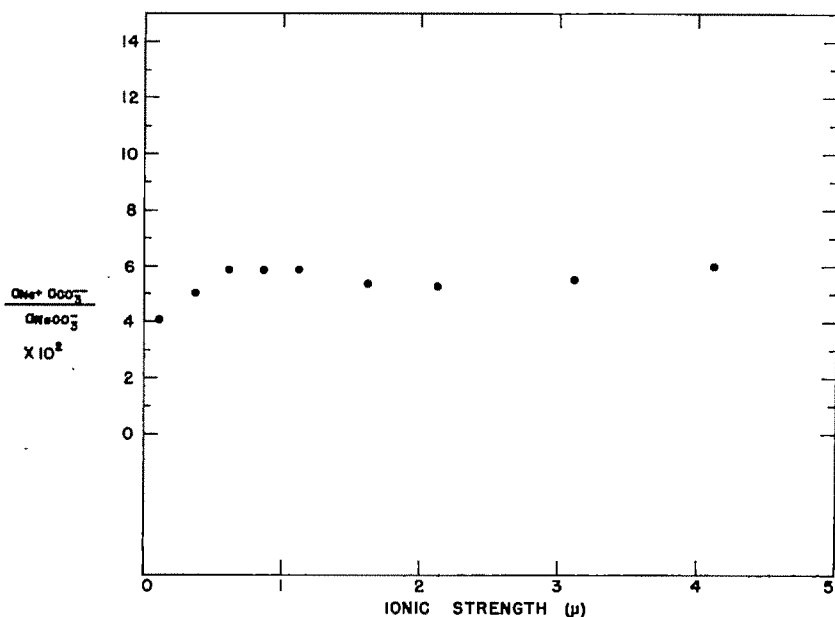


Fig. 6. $\frac{a_{\text{Na}^+} a_{\text{CO}_3^{--}}}{a_{\text{NaCO}_3^-}}$ versus ionic strength.

CO_3^{--} ACTIVITY IN SEA WATER

Sea water, which contains Na^+ and Mg^{++} as the chief cations, is now seen as a medium in which the activity of CO_3^{--} is controlled by these factors: (1) The reduction of activity by electrical interaction of individual ions, as expected in any solution of the ionic strength of sea water. (2) The reduction of activity by the formation of the moderately stable NaCO_3^- complex. (3) The reduction of activity by the formation of the more stable MgCO_3^0 ion pair complex. All of these effects contribute to reduce the activity of CO_3^{--} to about 2 percent of its total molality. In the absence of factors 2 and 3, the activity of CO_3^{--} would be about 20 percent of its molality. Furthermore, it is apparent that although $m_{\text{Mg}^{++(\text{aq})}}$ is small relative to $m_{\text{Na}^+(\text{aq})}$, the effect of the Mg^{++} in sea water is greater than that of Na^+ , owing to the greater stability of the magnesium complex.

It is possible, knowing the pH and the concentrations of Na^+ and Mg^{++} of sea water, and the CO_2 pressure of the atmosphere, to calculate, making use of the appropriate dissociation constants, how much of the total CO_3^{--} is complexed by Mg, how much by Na, and how much is free. These relations are used:

$$\begin{aligned}
 m_{\text{CO}_3^{--(\text{f})}} &= m_{\text{CO}_3^{--}} + m_{\text{NaCO}_3^-} + m_{\text{MgCO}_3^0} \\
 m_{\text{CO}_3^{--}} &= a_{\text{CO}_3^{--}} / \gamma_{\text{CO}_3^{--}} \\
 m_{\text{NaCO}_3^-} &= a_{\text{NaCO}_3^-} / \gamma_{\text{NaCO}_3^-} = \frac{a_{\text{Na}^+} a_{\text{CO}_3^{--}}}{5.4 \times 10^{-2} \gamma_{\text{NaCO}_3^-}} \\
 m_{\text{MgCO}_3^0} &= a_{\text{MgCO}_3^0} / \gamma_{\text{MgCO}_3^0} = \frac{a_{\text{Mg}^{++}} a_{\text{CO}_3^{--}}}{4 \times 10^{-4} \gamma_{\text{MgCO}_3^0}} \\
 a_{\text{CO}_3^{--}} &= \frac{10^{-10.83} a_{\text{HCO}_3^-}}{a_{\text{H}^+}} \\
 a_{\text{HCO}_3^-} &= \frac{10^{-7.82} a_{\text{H}_2\text{O}} a_{\text{CO}_2}}{a_{\text{H}^+}}
 \end{aligned}$$

We obtained by substituting the appropriate numbers* in the equations, $m_{\text{MgCO}_3^0} = 0.000216$, $m_{\text{NaCO}_3^-} = 0.000050$, and $m_{\text{CO}_3^{--}} = 0.000027$. Expressed as percentage of $m_{\text{CO}_3^{--(\text{f})}}$, these are $m_{\text{MgCO}_3^0} = 74$ percent, $m_{\text{NaCO}_3^-} = 17$ percent, and free $\text{CO}_3^{--} = 9$ percent.

The relative effects of K^+ , Na^+ , and Mg^{++} are qualitatively those expected from their charges and diameters. The large, singly charged K^+ (ionic potential = 0.75, cf. Mason, 1952, p. 138) apparently interacts slightly, if at all, with CO_3^{--} , even in solutions of high K^+ concentration. Na^+ (ionic potential = 1.0), on the other hand, although singly charged, bonds fairly strongly with CO_3^{--} , because of its smaller diameter. Small, doubly charged Mg^{++} (ionic potential = 2.6) is most effective in tying up CO_3^{--} .

Charge and sign are not the only variables controlling complex formation. As shown by Silman (1958, p. 67), Cu^{++} , although it is about the same size and charge as Mg^{++} , forms not only an ion pair CuCO_3^0 more stable than MgCO_3^0 ($K_{\text{CuCO}_3^0} = 10^{-6.77}$), but also complexes with CO_3^{--} as $\text{Cu}(\text{CO}_3)_2^{--}$, and as $\text{Cu}(\text{OH})_2\text{CO}_3^{--}$.

In summary, CO_3^{--} molality ($m_{\text{CO}_3^{--(\text{f})}}$) in sea water is highly sensitive to the $\text{Mg}^{++}/\text{Na}^+$ ratio, and any differential use of these two cations by organic or inorganic agents can be expected to affect $a_{\text{CO}_3^{--}}$ profoundly. The low $\gamma_{\text{CO}_3^{--(\text{f})}}$ value for sea water can be attributed chiefly to the formation of the ion pair MgCO_3^0 .

* The pH of sea water is taken as 8.2, atmospheric CO_2 pressure as $10^{-3.5}$ atmos., activity of H_2O in sea water as $10^{-0.01}$, and $\gamma_{\text{MgCO}_3^0}$ as 1.13. Activity coefficients for Na^+ , Mg^{++} , CO_3^{--} , and NaCO_3^- (assuming $\gamma_{\text{HCO}_3^-} = \gamma_{\text{NaCO}_3^-}$) are taken from figures 1, 3, and 4.

C. *Solubility of calcite in sea water.*—In sea water of pH 8.2 and at 20°C., the concentration of Ca^{++} is 0.01023, that of CO_3^{--} is 0.00026; the ion product is 2.66×10^{-6} (Sverdrup, 1942, p. 205).

The activity of CO_3^{--} at the ionic strength of sea water may be calculated from our values of $\gamma_{\text{CO}_3^{--}}$ in the NaCl-MgCl₂ mixture resembling sea water:

$$m_{\text{CO}_3^{--}} \times \gamma_{\text{CO}_3^{--}} = (2.6 \times 10^{-4}) (2.1 \times 10^{-2}) \\ = 5.5 \times 10^{-6} \quad (15)$$

Assuming that sea water is in equilibrium with the CO_2 of the atmosphere, the activity of CO_3^{--} can be calculated from the relations

$$\frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{P_{\text{CO}_2} a_{\text{H}_2\text{O}}} = 10^{-7.82}, \quad (16)$$

and

$$\frac{a_{\text{H}^+} a_{\text{CO}_3^{--}}}{a_{\text{HCO}_3^-}} = 10^{-10.33} \quad (17)$$

Multiplying (16) by (17),

$$\frac{a_{\text{H}^+}^2 a_{\text{CO}_3^{--}}}{P_{\text{CO}_2} a_{\text{H}_2\text{O}}} = 10^{-18.15}$$

Rearranging,

$$a_{\text{CO}_3^{--}} = \frac{10^{-18.15} P_{\text{CO}_2} a_{\text{H}_2\text{O}}}{a_{\text{H}^+}^2}$$

Substituting $10^{-8.5}$ for P_{CO_2} of the atmosphere, $10^{-8.2}$ for a_{H^+} , and $10^{-0.01}$ for $a_{\text{H}_2\text{O}}$

$$a_{\text{CO}_3^{--}} = 5.4 \times 10^{-6} \quad (18)$$

The value for $a_{\text{CO}_3^{--}}$ obtained in (18) is almost exactly the same as that in (15), and indicates approximate attainment of equilibrium of sea water with the atmosphere.

Taking the activity product of calcite as $10^{-8.35}$, we can calculate the activity of Ca^{++} in sea water.

$$a_{\text{Ca}^{++}} = \frac{10^{-8.35}}{a_{\text{CO}_3^{--}}} = \frac{4.5 \times 10^{-9}}{5.4 \times 10^{-6}} = 8.3 \times 10^{-4}.$$

Using the value of $\gamma_{\text{Ca}^{++}}$ at the ionic strength of sea water from figure 4, we can obtain $m_{\text{Ca}^{++}}$:

$$m_{\text{Ca}^{++}} = \frac{a_{\text{Ca}^{++}}}{\gamma_{\text{Ca}^{++}}} = \frac{8.3 \times 10^{-4}}{2.8 \times 10^{-1}} = 3.0 \times 10^{-3}.$$

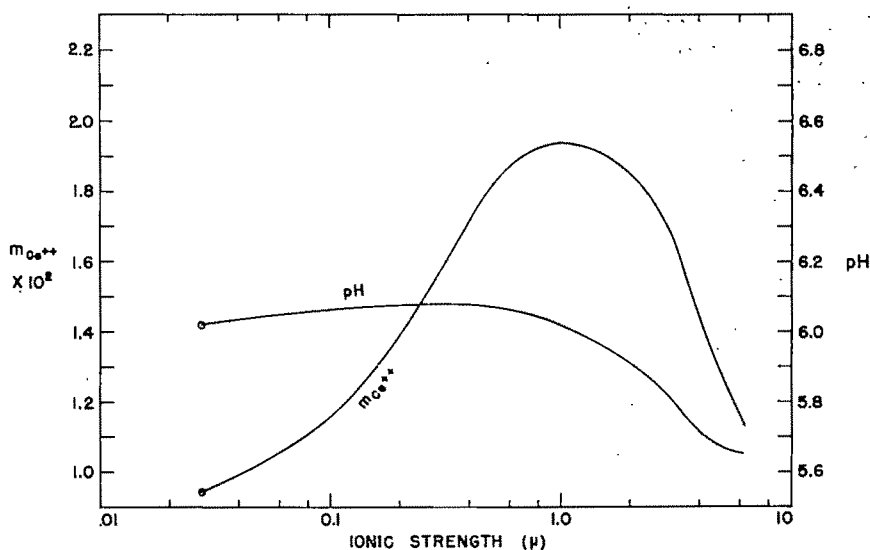


Fig. 7. Calculated values of $m_{Ca^{++}}$ and pH in NaCl solutions in equilibrium with calcite at $P_{CO_2} = 1$.

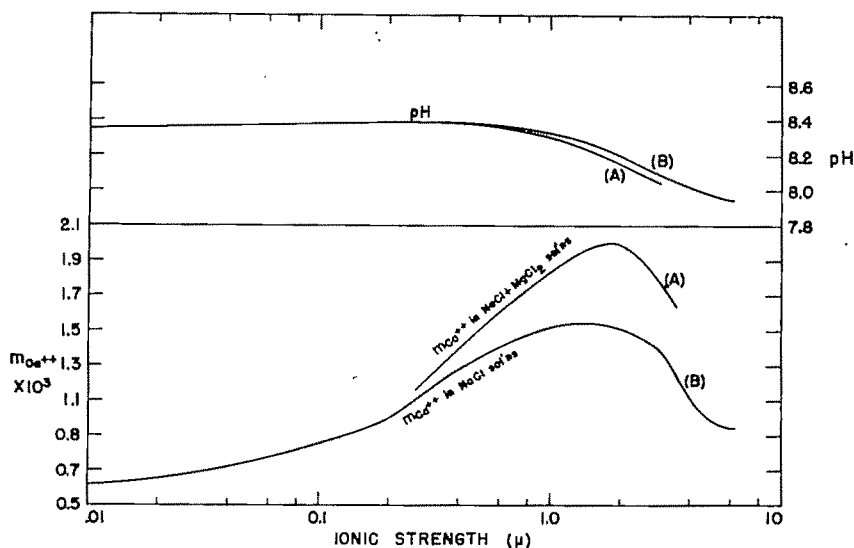


Fig. 8. Calculated values of $m_{Ca^{++}}$ and pH in NaCl solutions and in NaCl + $MgCl_2$ solutions in equilibrium with calcite at $P_{CO_2} = 10^{-3.5}$.

This value is about one-third of the observed calcium in sea water, and if no complexing of Ca^{++} occurs, it must be concluded that sea water is supersaturated with respect to calcite by about 300 percent. However, Greenwald (1941) reports a $CaCO_3^0$ ion pair that is approximately as stable as $MgCO_3^0$, and Bell and George (1953) report a $CaSO_4^0$ complex with a dissociation con-

stant of 4.9×10^{-8} . Still others may well exist, so that the supersaturation, if any, is less than 300 percent.

The discrepancy between values of K'_{CaCO_3} in sea water obtained by Revelle and Fleming and by Wattenberg and Timmerman (Sverdrup, 1942, p. 205) can be partly reconciled by careful attention to the way that K'_{CaCO_3} is defined. If K'_{CaCO_3} is taken as $(m_{\text{Ca}^{++}})(m_{\text{CO}_3^{--}})$, that is, the ion product, the value obtained, 2.66×10^{-6} , is very close to that of Revelle and Fleming, 2.4×10^{-6} . If, on the other hand, K'_{CaCO_3} is taken as the product of $m_{\text{Ca}^{++}}$ and $m_{\text{CO}_3^{--(\text{cr})}}$, we obtain the value 7.8×10^{-7} , and this is almost as small as that obtained by Wattenberg and Timmerman, 5.5×10^{-7} . Revelle and Fleming determined the concentration of Ca^{++} by direct analysis, whereas Wattenberg and Timmerman calculated Ca^{++} from alkalinity measurements. The difference between the results obtained by the two methods can be attributed to complexes of Ca^{++} .

Figure 7 shows calculated values for $m_{\text{Ca}^{++}}$ and pH in NaCl solutions in equilibrium with calcite at $P_{\text{CO}_2} = 1$.

Figure 8 shows calculated values for $m_{\text{Ca}^{++}}$ and pH in NaCl solutions and in NaCl + MgCl_2 solutions resembling sea water. The calculations are made assuming equilibrium with calcite, and CO_2 pressure about the same as that of air ($P_{\text{CO}_2} = 10^{-3.5}$). Note the marked increase in $m_{\text{Ca}^{++}}$ in "synthetic sea water" (NaCl + MgCl_2 solutions).

The presence of a maximum $m_{\text{Ca}^{++}}$ at intermediate ionic strengths in both figures 7 and 8 may be of use in explaining solution and cementation effects in subsurface waters.

SUMMARY

- (1) Activity coefficients of HCO_3^- and CO_3^{--} ions were obtained in NaCl, MgCl_2 , and NaCl- MgCl_2 solutions over a wide range of ionic strength.
- (2) Marked differences in the activity coefficient values obtained at the same ionic strengths in the various solutions are attributed to the formation of complexes of Na^+ and Mg^{++} with HCO_3^- and CO_3^{--} . No appreciable complexing seems to occur in solutions containing only potassium salts.
- (3) The complexes formed by interaction of cations with bicarbonate ion could not be satisfactorily characterized.
- (4) The dissociation constants of the complexes formed by interaction of Na^+ and Mg^{++} with carbonate ion are:

$$\frac{a_{\text{Na}^+} a_{\text{CO}_3^{--}}}{a_{\text{NaCO}_3^-}} = 5.6 \times 10^{-2}$$

$$\frac{a_{\text{Mg}^{++}} a_{\text{CO}_3^{--}}}{a_{\text{MgCO}_3^0}} = 4.0 \times 10^{-4}$$

(5) The total concentration of carbonate ion in sea water can be calculated by assuming that sea water is in equilibrium with the partial pressure of carbon dioxide of the atmosphere, and that the only contributions to its concentration are $m\text{CO}_3^{--}$, $m\text{NaCO}_3^-$, and $m\text{MgCO}_3^0$.

(6) Complexing of carbonate ion has a marked effect on the solubility of carbonate minerals. The relatively high stability of the MgCO_3^0 ion pair indicates that magnesium exerts an important indirect control on CaCO_3 solubility.

(7) The Na^+ and Mg^{++} interaction with CO_3^{--} and HCO_3^- also exert important controls on the total dissolved carbonate in sea water. If the ocean had NaCl substituted for MgCl_2 , the total concentration of CO_3^{--} would diminish to 20 percent of its present value, and total HCO_3^- would drop to about 80 percent. The result would be a major redistribution of CO_2 between atmosphere and ocean.

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THE SYSTEM $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$ *

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ABSTRACT. Results of quenching experiments on mixtures lying along the $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$ join of the CaO--MnO--SiO_2 system are presented. The oxygen partial pressure was controlled to maintain manganese as Mn^{2+} . The system $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$ is not entirely binary because of the incongruent melting of a range of compositions to $(\text{Ca,Mn})\text{O}$ solid solutions and liquid. The departure from binary melting behavior is, however, slight.

Liquidus temperatures drop sharply from Ca_2SiO_4 ($\sim 2130^\circ$) to a liquidus invariant point at 1375° involving: liquid (45.5 wt.% Mn_2SiO_4), $\alpha\text{Ca}_2\text{SiO}_4$, and $\alpha'\text{Ca}_2\text{SiO}_4$ solid solutions. With further increase in Mn_2SiO_4 , liquidus temperatures fall more slowly to another invariant point involving $\alpha'\text{Ca}_2\text{SiO}_4$, tephroite (Mn_2SiO_4) solid solutions, and liquid (72% Mn_2SiO_4) at 1257° ; and thence through a minimum at 75.5% Mn_2SiO_4 and 1204° , before rising to the tephroite end at 1345° .

The compound CaMnSiO_4 (glaucochroite) forms a complete series of solid solutions with tephroite and a limited series of solid solutions with Ca_2SiO_4 . $\gamma\text{Ca}_2\text{SiO}_4$ and Mn_2SiO_4 are not completely miscible.

INTRODUCTION

Previous studies of the $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$ system are very incomplete. Kallenberg (1914) and Toklody (1928) have approximately determined parts of the solidus and liquidus curves. These studies are inadequate by current standards. Therefore, the system $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$ has been reinvestigated to determine the equilibrium relationships more exactly.

EXPERIMENTAL PROCEDURE

The experimental procedure used in phase rule studies of silicate systems has been described in detail, for example, by Day, Shepherd, and Wright (1906). Therefore, only a brief description of the procedures used, with special reference to the study of manganous oxide systems, will be given.

Starting materials consisted of the best commercially available grades of CaCO_3 , MnO_2 , and silicic acid. These starting materials were dried at 250°C , 105°C , and 1350°C , respectively, and stored in a desiccator prior to use. The MnO_2 was analyzed chemically for Mn content to check for possible non-stoichiometry.

Mixtures were prepared by fusing weighed batches of CaCO_3 , MnO_2 , and SiO_2 in platinum crucibles. The fusion was done either in air or in a gas-air furnace having a reasonably oxidizing atmosphere. This procedure prevents appreciable loss of manganese through alloying with the platinum. The fused charges were quenched, yielding a glass or partly devitrified glass. This was crushed in a steel mortar to pass 40 mesh, and any iron filings removed with a powerful magnet. Some mixtures—those having liquidus temperatures in excess of 1550°C —were sintered below the anticipated solidus temperature. The sintering was repeated with intermediate grindings until a product of satisfactory homogeneity was obtained.

Runs were made in vertical tube, platinum-wound furnaces. With a suitable controller, temperature regulation on the order of $\pm 1.5^\circ\text{C}$ was achieved. Temperature readings were made using Pt-Pt10Rh thermocouples. These were

* Contribution No. 58-95, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

calibrated frequently against two or more materials of known melting point, including: gold (1063°C), $\text{CaMg}(\text{SiO}_3)_2$ (1391.5°C), and CaSiO_3 (1544°C). Temperatures reported here are believed accurate to about $\pm 2^{\circ}\text{C}$.

The condensed phases present in quench runs were identified by transmitted and reflected light microscopy and by X-ray powder diffraction patterns.

Hydrothermal runs were made as an aid in studying subsolidus equilibria. The hydrothermal apparatus used is essentially that described by Tuttle (1948).

In studying manganese oxide systems, it is important to control the oxidation state of manganese. Quench runs reported here were made in an atmosphere of low oxygen partial pressure, generated by passing a slow stream of premixed carbon dioxide-hydrogen gas through the furnace tube. The general techniques for working at reduced partial oxygen pressures have been described recently by Muan (1958) and, with particular reference to the study of manganous oxide systems, by Glasser (1958).

A slightly different technique must be employed for making hydrothermal runs under reducing conditions, because of the difficulty of supplying an atmosphere of low oxygen partial pressure from an external source. The proper atmosphere is generated internally by adding an open packet of manganese metal to the bomb. Powdered manganese metal reacts rapidly with water at elevated temperatures and thus controls the oxygen pressure in the bomb.

TABLE 1
Critical quench runs in the system $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$

Ca_2SiO_4	Wt.% Mn_2SiO_4	Temp. $^{\circ}\text{C}$	Time hours	Phases Present*
5.0	95.0	1335	2	Teph. s.s. (tr.) + L.
"	"	1298	2	Teph. s.s. + L.
"	"	1287	2	Teph. s.s.
10.0	90.0	1330	20	L.
"	"	1323	2	Teph. s.s. + L.
"	"	1285	2	Teph. s.s. + L.
"	"	1274	2	Teph. s.s. + Ox. s.s. + L.
"	"	1255	2	Teph. s.s. + Ox. s.s. + L.
"	"	1241	3	Teph. s.s.
12.0	88.0	1326	2	L.
"	"	1314	2	Teph. s.s. + L.
"	"	1289	2	Teph. s.s. + L.
"	"	1274	2	Teph. s.s. + Ox. s.s. + L.
"	"	1247	2	Teph. s.s. + Ox. s.s. + L.
"	"	1239	12	Teph. s.s.
16.0	84.0	1305	2	L.
"	"	1290	3	Teph. s.s. + L.
"	"	1280	3	Teph. s.s. + L.
"	"	1270	2	Teph. s.s. + Ox. s.s. + L.
"	"	1212	2	Teph. s.s. + Ox. s.s. + L. (tr.)
"	"	1206	2	Teph. s.s.
20.0	80.0	1278	12	L.
"	"	1274	14	L. + Ox. s.s. (tr.)
"	"	1269	12	Teph. s.s. + Ox. s.s. + L.

TABLE 1 (Continued)

Ca ₂ SiO ₄	Wt. % Mn ₂ SiO ₄	Temp. °C	Time hours	Phases Present*
22.0	78.0	1282	2	L.
"	"	1274	2	L. + Ox. s.s. (tr.)
"	"	1250	12	L. + Ox. s.s.
"	"	1235	2	Teph. s.s. + Ox. s.s. + L.
"	"	1210	2	Teph. s.s. + Ox. s.s. + L.
"	"	1196	4	Teph. s.s.
26.0	74.0	1239	10	L. + Ox. s.s.
"	"	1219	2	Teph. s.s. + Ox. s.s. + L.
"	"	1208	2	Teph. s.s. + Ox. s.s. + L.
"	"	1201	2	Teph. s.s.
30.0	70.0	1296	10	L.
"	"	1285	6	L. + Ox. s.s.
"	"	1274	4	α' s.s. + Ox. s.s. + L.
"	"	1259	2	α' s.s. + Ox. s.s. + L.
"	"	1241	2	Teph. s.s. + Ox. s.s. + L.
"	"	1219	2	Teph. s.s. + Ox. s.s. + L.
"	"	1205	12	Teph. s.s.
35.0	65.0	1304	2	L.
"	"	1295	2	α' s.s. + L.
"	"	1285	2	α' s.s. + Ox. s.s. + L.
"	"	1220	12	Teph. s.s. + Ox. s.s. + L.
"	"	1216	2	Teph. s.s.
40.0	60.0	1310	2	L.
"	"	1304	2	α' s.s. + L.
"	"	1299	12	α' s.s. + L.
"	"	1282	2	α' s.s. + Ox. s.s. + L.
"	"	1263	2	α' s.s. + Ox. s.s. + L.
"	"	1254	3	Teph. s.s. + Ox. s.s. + L.
"	"	1224	3	Teph. s.s. + L. (tr.?)
46.2	53.8	1324	2	α' s.s. (tr.) + L.
"	"	1292	2	α' s.s. + L.
"	"	1276	2	α' s.s. + Ox. s.s. + L.
"	"	1272	12	α' s.s. + Ox. s.s. + L.
"	"	1257	2	α' s.s. + Teph. s.s. + Ox. s.s. + L.
"	"	1239	2	Teph. s.s. + Ox. s.s. + L.
"	"	1231	2	Teph. s.s.
50.0	50.0	1344	2	L.
"	"	1336	2	α' s.s. + L.
"	"	1269	3	α' s.s. + Ox. s.s. + L.
"	"	1255	3	Teph. s.s. + Ox. s.s. + L.
"	"	1241	2	Teph. s.s. + Ox. s.s. + L. (tr.)
54.0	46.0	1379	2	L.
"	"	1360	2	α' s.s. + L.
"	"	1262	3	α' s.s. + Ox. s.s. + L.
"	"	1255	2	Teph. s.s. + Ox. s.s. + L.
"	"	1249	3	Teph. s.s. + Ox. s.s. + L.
"	"	1239	2	Teph. s.s.
57.0	43.0	1514	2	L.
"	"	1475	2	α s.s. + L.
"	"	1382	3	α s.s. + L.
"	"	1367	2	α' s.s. + L.
"	"	1252	12	Teph. s.s. + L. (tr.)
"	"	1248	24	Teph. s.s.

TABLE 1 (Continued)

Ca_2SiO_4	Wt.% Mn_2SiO_4	Temp. °C	Time hours	Phases Present*
60.0	40.0	1550	2	α s.s. + L.
"	"	1384	2	α s.s. + L.
"	"	1374	4	α' s.s. + L.
"	"	1268	3	α' s.s. + Ox. s.s. + L.
"	"	1256	2	α' s.s. + Teph. s.s. + Ox. s.s. + L.
"	"	1247	2	α' s.s. + Teph. s.s.
"	"	1206	24	α' s.s. (tr.) + Teph. s.s.
"	"	1100	24	Teph. s.s.
65.0	35.0	1503	2	α s.s. + L.
"	"	1383	12	α s.s. + L.
"	"	1376	3	α s.s. + α' s.s. + L.
"	"	1363	2	α' s.s. + L.
"	"	1256	2	α' s.s. + Teph. s.s. + L. (tr.)
"	"	1247	2	α' s.s. + Teph. s.s.
"	"	1107	20	α' s.s. + Teph. s.s.
70.0	30.0	1545	1	α s.s. + L.
"	"	1376	3	α s.s. + α' s.s. + L.
"	"	1363	2	α' s.s. + L.
"	"	1271	12	α' s.s. + Ox. s.s. + L.
"	"	1265	2	α' s.s.
"	"	1243	10	α' s.s.
"	"	1160	20	α' s.s. + Teph. s.s.
"	"	1110	24	α' s.s. + Teph. s.s.
80.0	20.0	1550	1	α s.s. + L.
"	"	1383	2	α s.s. + L.
"	"	1358	12	α' s.s. + L.
"	"	1343	2	α' s.s.
"	"	1100	24	α' s.s.
90.0	10.0	1553	1	α s.s.
"	"	1406	3	α s.s.
"	"	1394	2	α' s.s.

Hydrothermal runs

Wt.% Mn_2SiO_4	Time days	Temp. °C	Pressure Kg./cm ²	Phases Present	Comment
35.0	1	900	400	Teph. s.s. + βCaS s.s. (tr.)	
"	7	730	1000	Teph. s.s.	
"	6	605	1000	" "	
"	6	495	1000	" "	
30.0	1	900	400	Teph. s.s. + βCaS s.s.	Dusted
"	3	850	600	γCaS s.s. + βCaS s.s. (tr.)	
"	7	730	1000	γCaS s.s. + Teph. s.s.	
"	6	605	1000	CaSH + Teph. s.s.	
"	7	600	200	CaSH + Teph. s.s.	
"	6	495	1000	CaSH + Teph. s.s.	
20.0	1	900	400	βCaS s.s. + CaS s.s.	Dusted
"	2	830	600	" " + " "	
"	5	775	600	γCaS s.s.	Dusted
"	7	610	900	CaSH + CaS s.s.	
"	6	495	1000	CaSH + Teph. s.s.	
10.0	2	830	600	βCaS s.s. + CaS s.s.	Dusted
"	5	775	600	" " + " "	
"	8	725	800	γCaS s.s. + CaSH	

* Abbreviations used: Teph. = Tephroite; CaS = Ca_2SiO_4 ; CaSH = dicalcium silicate hydrate; Ox = $(\text{Ca},\text{Mn})\text{O}$; L. = liquid; tr. = trace; s.s. = solid solution.

RESULTS

A phase diagram for the system $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$ (fig. 1) summarizes the results obtained. The diagram is based on quench runs; representative runs are shown in table 1.

Some important features of this diagram are as follows: the system is not completely binary. A range of compositions extending from f to i (fig. 1) melt incongruently to $(\text{Ca},\text{Mn})\text{O}$ solid solutions and liquid. This $(\text{Ca},\text{Mn})\text{O}$ phase will be referred to as "oxide solid solution". Other ranges of compositions extending from e to f and from i to j exhibit partial incongruent melting.¹ The quantity of oxide solid solution produced by this incongruent melting is small. This has been shown by studies in the ternary system CaO--MnO--SiO_2 .² Therefore, the error produced by projecting the results on the orthosilicate temperature-composition section is not serious and greatly simplifies presentation of the data. In figure 1, nonbinary phenomena are indicated by lighter weight lines, binary phenomena by heavier weight lines.

Four series of Ca_2SiO_4 solid solutions have been encountered. Three of these solid solutions, designated as α , α' , and γ according to current usage, are stable solid solution series. The fourth, β series, forms metastably from inversion of α and $\alpha'\text{Ca}_2\text{SiO}_4$ and its solid solutions upon cooling from high temperatures. Although the high temperature forms invert partly or wholly on cooling, the former presence of α or α' solid solutions can be recognized from the characteristic appearance of the charge on microscopic examination and the limits of solid solution with Mn_2SiO_4 thus established. Maximum solubility of Mn_2SiO_4 in the α form is 19% Mn_2SiO_4 (point d); in the α' form 31.5% Mn_2SiO_4 (point g).

Olivine solid solutions extend over a wider compositional range. Two series of olivine solid solutions are present. One of these is based on tephroite (Mn_2SiO_4), the other on $\gamma\text{Ca}_2\text{SiO}_4$. The tephroite solid solution series is the more extensive, extending along the solidus from Mn_2SiO_4 to point h (fig. 1). This point represents the most calcic olivine stable in contact with liquid.

Replacement of Mn^{++} by Ca^{++} in the tephroite structure leads to formation of an ordered 1:1 type olivine, CaMnSiO_4 . This olivine is known from natural occurrences as the mineral glaucochroite. Mn_2SiO_4 and CaMnSiO_4 form a complete series of solid solutions. Also, CaMnSiO_4 can take considerable Ca_2SiO_4 into solid solution. This is shown by the curve extending downward from point h, marking the calcium-rich limit of tephroite solid solutions.³

¹ On heating compositions ranging from e to f through their melting interval, the initial phases produced at or just above the solidus are: olivine solid solution, oxide solid solution, and liquid. Thus the initial melting is incongruent. On continued heating, however, the oxide solid solution is resorbed, the last trace disappearing at 1290°C. In the remainder of the melting interval, the melting phenomena encountered are entirely binary in nature. The same behavior characterizes the melting of compositions from i to j, except that the melting phenomena encountered become completely binary above 1275°C. Thus points f and i represent limiting cases in the transition between compositions melting incongruently and melting partly incongruently, just as points e and j represent the case of transitions between partly incongruently and congruently melting compositions. The points e, f, i, and j are not invariant points.

² Unpublished data of F. P. Glasser.

³ Because the field of olivine solid solutions based on tephroite sweeps past the 1:1 composition, these olivines are referred to as tephroite solid solutions. The special nature of the 1:1 composition will be discussed in a later section.

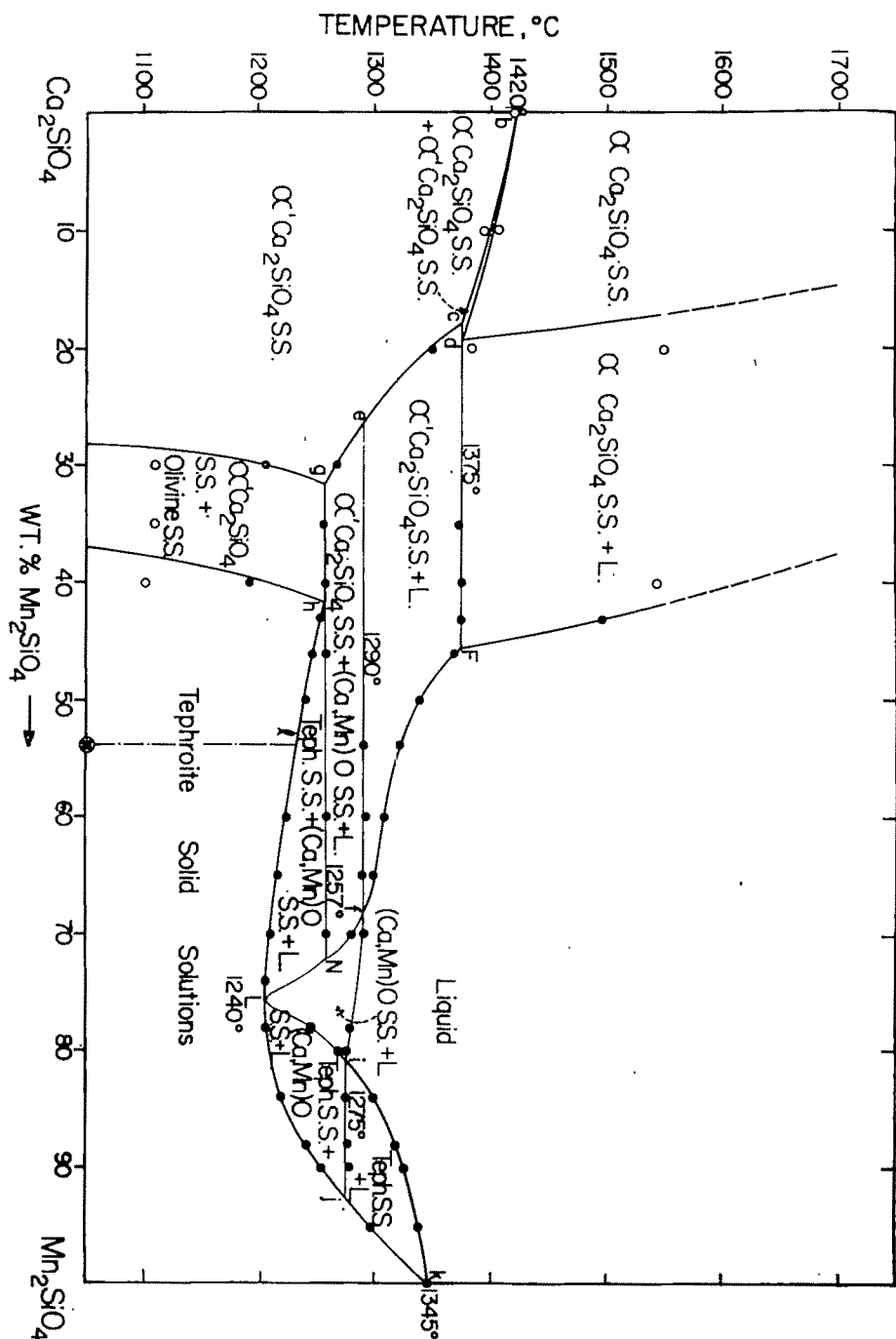


Fig. 1. Phase equilibrium relations in the system $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$. Binary relations are shown by heavier weight lines, nonbinary relations by lighter weight lines. Dashed lines indicate that the relations shown are approximate. Solid dots indicate the mean of critical quench runs; hollow dots represent individual runs. The dot-dash vertical line marks the glaucocroite composition. Temperatures and location of binary invariant points are shown in table 2.

This curve includes in the tephroite field a range of compositions much richer in Ca than the glaucocroite composition. This curve, together with the similar curve extending downward from point g, marks the relatively narrow two-phase region separating the fields of homogeneous α' solid solutions and olivine solid solutions. The phase relations existing at lower temperatures, involving equilibrium between $\gamma\text{-Ca}_2\text{SiO}_4$ and the manganese olivine solid solutions, are discussed on a later page.

Liquidus temperatures drop very rapidly from Ca_2SiO_4 ($\sim 2130^\circ$) to a liquidus invariant point at 1375° (point F, fig. 1). Beyond this point liquidus temperatures continue to drop but much less rapidly. If the incongruent melting phenomenon be neglected, the liquidus profile follows the curve FfNLik, passing through an invariant point (N, fig. 1) marking the intersection of the olivine- $\alpha'\text{-Ca}_2\text{SiO}_4$ inversion with the liquidus profile, and thence to a minimum (L) at 1204° . The liquidus profile then rises again toward the melting point of tephroite (1345°).

The temperature of critical liquidus points and the composition of phases present are given in table 2.

TABLE 2
Critical liquidus points in the system $\text{Ca}_2\text{SiO}_4\text{-Mn}_2\text{SiO}_4$

Designation Fig. 1	Nature of Point	Phases Present*	Temp. $^\circ\text{C}$	Remarks**
—	M.P.	$\alpha\text{CaS} + \text{L}$	~ 2130	M.P. of Ca_2SiO_4
F	Invariant	$\alpha\text{CaS}, \alpha'\text{CaS} + \text{L}$	1375	$\alpha\text{CaS} = 19\%$ $\alpha'\text{CaS} = 18\%$ $\text{L} = 45.5\%$
N	Invariant	$\alpha'\text{CaS}, \text{Teph.}, \text{L}$	1257	$\alpha'\text{CaS} = 31.5\%$ $\text{Teph.} = 41.5\%$ $\text{L} = 72\%$
L	Minimum	$\text{Teph. s.s.} + \text{L}$	1204	$\text{L} = 75.5\%$
k	M.P.	$\text{Teph.} + \text{L}$	1345	M.P. of Mn_2SiO_4

* Abbreviations used: $\text{CaS} = \text{Ca}_2\text{SiO}_4$; L = Liquid; Teph. = Tephroite.

** Compositions given in percentages are in weight percent Mn_2SiO_4 .

DISCUSSION OF RESULTS

Equilibrium between Ca_2SiO_4 solid solutions.—Manganese is a relatively poor stabilizer for the high temperature forms of Ca_2SiO_4 . Despite extensive solid solution of Mn_2SiO_4 in both α and $\alpha'\text{-Ca}_2\text{SiO}_4$, the manganese-rich Ca_2SiO_4 solid solutions "dust" on quenching just as pure Ca_2SiO_4 does. In only a few cases—particularly in mixtures containing appreciable liquid— $\alpha'\text{-Ca}_2\text{SiO}_4$ solid solutions have been partly preserved to room temperature. This behavior makes recognition of the high temperature equilibria rather difficult. The "dusting" of quench charges in this composition range precludes making polished sections. With sufficient experience, however, it was found possible to make a consistent interpretation of the results of quenching experiments. The interpretation was aided by several factors. A wide range of liquid compositions in this system can be quenched to yield glasses which survive the "dusting" of the charge. Only in the vicinity of the liquidus minimum was serious difficulty encountered: these liquid compositions tended to devitrify rapidly upon

quenching. In quench charges which had dusted on cooling, glass or even devitrified glass could be recognized in small quantities, thus allowing accurate location of solidus curves. Runs which were entirely liquid (and hence free from the seeding action of primary crystals) tended to quench to good glasses, thus facilitating location of the liquidus curves.

$\alpha\text{Ca}_2\text{SiO}_4$ and its solid solutions have not been quenched to room temperature. Nevertheless, distinction between former α and α' solid solutions may be made, and the temperature of the line dF (fig. 1) located, from the appearance of the quenched crystals, as well as from the intersection of solidus and liquidus curves bounding the fields of the pertinent Ca_2SiO_4 solid solutions plus liquid. Crystals of $\alpha'\text{Ca}_2\text{SiO}_4$ solid solutions are characterized by sets of fine twin lamellae. Although the $\alpha'\text{Ca}_2\text{SiO}_4$ solid solutions may invert on quenching, the lamellar twinning is still preserved. This type of twinning has never been observed as a feature of primary olivine solid solutions, and is thus indicative of inversion from the α' form. Inverted $\alpha'\text{Ca}_2\text{SiO}_4$ solid solutions usually exhibit the optical properties of $\beta\text{Ca}_2\text{SiO}_4$ solid solutions, or a mixture of $\beta\text{Ca}_2\text{SiO}_4$ and olivine solid solutions.

$\alpha\text{Ca}_2\text{SiO}_4$ solid solutions are distinguished by preservation of a well-developed set of hexagonal cleavages. Superimposed on these cleavages are the features impressed by the subsequent series of inversions occurring on quenching. That is, on examination at room temperature, a former crystal of $\alpha\text{Ca}_2\text{SiO}_4$ solid solution retains the hexagonal (or pseudohexagonal) crystal habit and cleavage of that form, the twinning of the α' form, and the optical properties of mixtures of β and $\gamma\text{Ca}_2\text{SiO}_4$ solid solutions and olivine solid solutions.

Compound formation.—Two intermediate compounds have been reported as occurring in this system. Goldschmidt and Rait (1943) reported the syn-

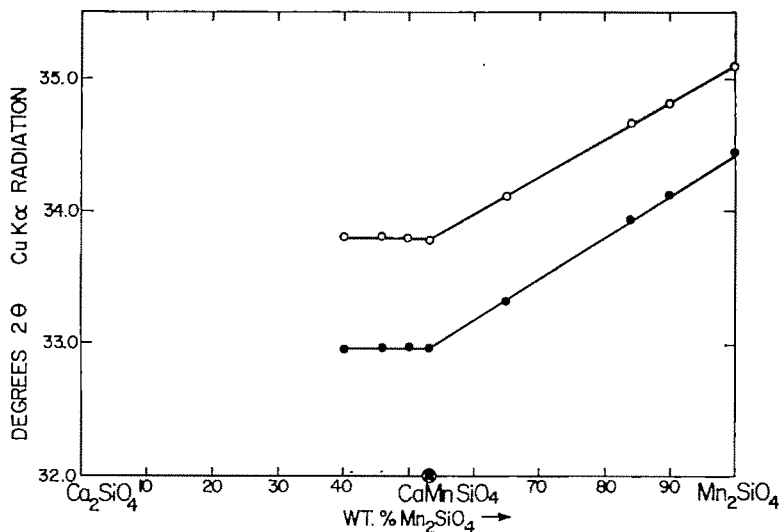


Fig. 2. Location of the (112) and (131) X-ray reflections (upper and lower lines, respectively) as a function of olivine composition. Values are corrected to absolute by an internal quartz standard. Experimental points are shown by small circles.

thesis of a "manganese merwinite", $\text{Ca}_3\text{Mn}(\text{SiO}_4)_2$, by heating this composition to 1400°C in a hydrogen atmosphere. Identification was made from the X-ray powder pattern of the resulting preparation. No similar results were obtained in this study. The composition $\text{Ca}_3\text{Mn}(\text{SiO}_4)_2$, after heating to 1400°C , quenches to give a mixture of various Ca_2SiO_4 solid solutions (β , γ , and, with sufficiently rapid quenching, α'). Mixtures of these Ca_2SiO_4 solid solutions have X-ray powder patterns closely resembling that of merwinite itself, but shifted toward larger d-spacing values. Optical examination of the quenched charges reveals the several phases present, and careful examination of the X-ray powder patterns obtained gives an interpretation consistent with the optical data. Hydrothermal runs made at lower temperatures have also failed to yield a merwinite-like phase. It is believed that Goldschmidt and Rait's interpretation of the X-ray powder pattern was in error. From figure 1, the composition $\text{Ca}_3\text{Mn}(\text{SiO}_4)_2$ should consist of $\alpha'\text{Ca}_2\text{SiO}_4$ solid solution and liquid at 1400°C .

The compound CaMnSiO_4 was first reported as a naturally occurring mineral and named glaucochroite by Penfield and Warren (1899). Later X-ray studies by O'Daniel and Tscheischwili (1942) and O'Mara (1951) confirm the identity of CaMnSiO_4 as a separate compound. The reported structure contains two calcium and two manganese atoms per unit cell, with the calcium and manganese atoms arranged in ordered fashion. In a later investigation, however, O'Daniel and Tscheischwili (1943) concluded that glaucochroite was a member of an uninterrupted $\gamma\text{Ca}_2\text{SiO}_4\text{-Mn}_2\text{SiO}_4$ solid solution series and had no status as a separate compound.

The evidence presented here supports the identity of glaucochroite as a separate compound. From figure 1 it can be seen that a wide range of compositions yield a homogeneous olivine solid solution. The properties of the olivine solid solutions obtained, when plotted as a function of composition, show definite breaks at the glaucochroite composition. For example, the (112) and (131) X-ray reflections of olivine solid solutions were measured. Figure 2 shows the location (2θ) of these reflections, as a function of olivine composition. Starting from Mn_2SiO_4 , the substitution of Ca^{++} for Mn^{++} shifts the position of the reflections to lower 2θ (higher d-spacing) values, as might be expected from the relative ionic sizes of Ca^{++} (1.06 Å) and Mn^{++} (0.91 Å). Compositions richer in Ca^{++} than the glaucochroite composition show little further shift in lattice parameters.

Although results are shown for two selected reflections only, all the reflections show the same behavior. Comparison of powder patterns of the olivine solid solutions taken over the range of 2θ values $70^\circ\text{-}20^\circ$ (Cu radiation) show that all the stronger reflections exhibit the same pattern of shift in d-spacing versus composition.

The trend of changes in observed lattice parameters for the olivines lying between Mn_2SiO_4 and CaMnSiO_4 , if extrapolated to the Ca_2SiO_4 composition, gives results in close agreement to the lattice parameters of $\gamma\text{Ca}_2\text{SiO}_4$. The actual parameters of olivine solid solutions lying between CaMnSiO_4 and the calcium-rich limit of the tephroite-glaucochroite olivines do not, however, lie on this extrapolation. The conclusion of O'Daniel and Tscheischwili (1943)

that glaucochroite was an arbitrarily selected composition in an uninterrupted $\gamma\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$ solid solution series was based on a comparison of unit cell sizes of three members of the solid solution series having the composition $\gamma\text{Ca}_2\text{SiO}_4$, Mn_2SiO_4 , and CaMnSiO_4 . Without the advantage of having a series of preparations of known composition, or at least a series of analyzed calcium-rich natural glaucochroites, their assumption seemed quite justifiable. Greer (1932) has also reported preparation of a complete series of solid solutions between $\gamma\text{Ca}_2\text{SiO}_4$ and Mn_2SiO_4 . Greer did, however, report difficulties in preparing homogeneous solid solutions in the compositional range, which in this study lies in the miscibility gap between the two olivine phases.

The break in unit cell parameters at the 1:1 mole composition may be compared with the refractive indices of olivine solid solutions (fig. 3). Substitution of Mn^{++} by Ca^{++} causes a rapid decrease in refractive indices, as might be expected. The accuracy of measuring the α and γ index of individual crystals (about $\pm .002$ to $\pm .003$ for the higher indices) is not sufficient to prove that a break exists at the 1:1 composition. The data suggest, however, that a slight break exists, and this is shown in figure 3. The refractive indices of the olivine solid solutions depend primarily on the Ca/Mn ratio; any structural contribution due to ordering of Ca^{++} and Mn^{++} is swamped by the

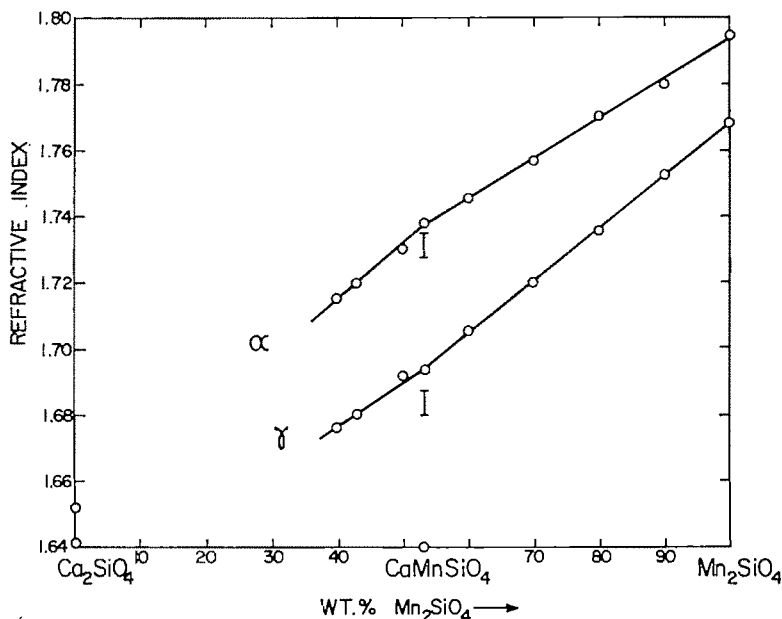


Fig. 3. Refractive indices of tephroite solid solutions. The top line represents the γ index; the lower line, the α index. Indices were determined with sodium light to an accuracy of about $\pm .002$ below $n = 1.700$, and about $\pm .003$ for indices above 1.700. The values obtained are plotted against weight percent composition as this gives nearly a straight line relation for compositions between CaMnSiO_4 and Mn_2SiO_4 . The α and γ indices of Ca_2SiO_4 are shown as small open circles; the experimentally determined indices of olivine solid solutions are shown by solid circles. The range of α and γ indices of five natural glaucochroites are shown by vertical lines terminated by a horizontal bar to indicate possible variation in composition, as well as in refractive index.

greater effect of compositional changes. These facts are considered sufficient to establish the identity of glaucochroite as a true compound.

It might be supposed that the intersection of the glaucochroite composition with the solidus would produce a discontinuity on the solidus curve at point *l*, figure 1. This is not the case however; any construction used must be compatible with the experimental observations—that a continuous series of tephroite solid solutions extends along the solidus from Mn_2SiO_4 to point *l* (fig. 1), and that solidus and liquidus curves do not touch at point *l*. It is not possible, therefore, to have a discontinuity on the solidus at point *l*. Solid solutions between *h* and *l*, and between *l* and Mn_2SiO_4 , are not different ranges of solid solutions but differ only in the rate of change in properties (see figs. 2 and 3). Therefore the correct thermodynamic expression of this is to make point *l* an inflection point on the solidus curve. The solidus curve marking the beginning of melting of olivine solid solutions passes smoothly through the glaucochroite composition.

The optical and X-ray data shown in figures 2 and 3 are taken from synthetic samples. Natural glaucochroite from Franklin Furnace, New Jersey has a powder pattern identical with that of synthetic CaMnSiO_4 . The refractive indices of the natural material are often substantially less than the synthetic material. This is shown in figure 3 where the α and γ indices of three samples of glaucochroite cited by Palache (1935, p. 75-80), and two samples of glaucochroite examined by the author,⁴ are shown. The range of α and γ indices of the five specimens are shown by straight vertical lines, with horizontal cross lines, representing the approximate upper and lower range of indices for the five specimens. The compositions are assumed to be at the ideal glaucochroite formula. This assumption is supported reasonably well by chemical analysis of several of the specimens. It is expected, however, that with sufficient diligence the entire olivine solid solution series from tephroite to the calcium-rich limit of solid solutions could be found in nature. Thus considerable variation in the composition and refractive indices of natural "glaucochroites" might be expected. Other substitutions, such as Mg, Fe, Zn, and Pb for Ca and Mn, will also have a strong influence on the refractive indices of natural glaucochroites, as these are common substituents in the natural minerals.

Subsolidus relations between Ca_2SiO_4 and Mn_2SiO_4 .—Phase relations between $\alpha'\text{Ca}_2\text{SiO}_4$ solid solutions, $\gamma\text{Ca}_2\text{SiO}_4$ solid solutions, and tephroite solid solutions are shown schematically in figure 4. This figure summarizes the results of dry and hydrothermal runs. Some of the difficulties encountered in determining equilibrium relations in this area may be discussed with reference to this figure. The inversion temperature between $\alpha'\text{Ca}_2\text{SiO}_4$ and $\gamma\text{Ca}_2\text{SiO}_4$ is shown as rising with addition of Mn_2SiO_4 . The rapid inversion of $\alpha'\text{Ca}_2\text{SiO}_4$ solid solutions on cooling produces the well-known "dusting" phenomena. Former $\alpha'\text{Ca}_2\text{SiO}_4$ solid solutions may be recognized in quench charges by two means: the "dusting" of these charges on quenching, and the presence of some $\beta\text{Ca}_2\text{SiO}_4$ solid solution as a product of this rapid inversion. Such a method does not permit accurate location of the inversion temperature of Mn_2SiO_4 .

⁴ These samples were kindly furnished by the Smithsonian Institution. Smithsonian sample numbers were R3494 (Gage Collection) and C6172 (Bauer Collection).

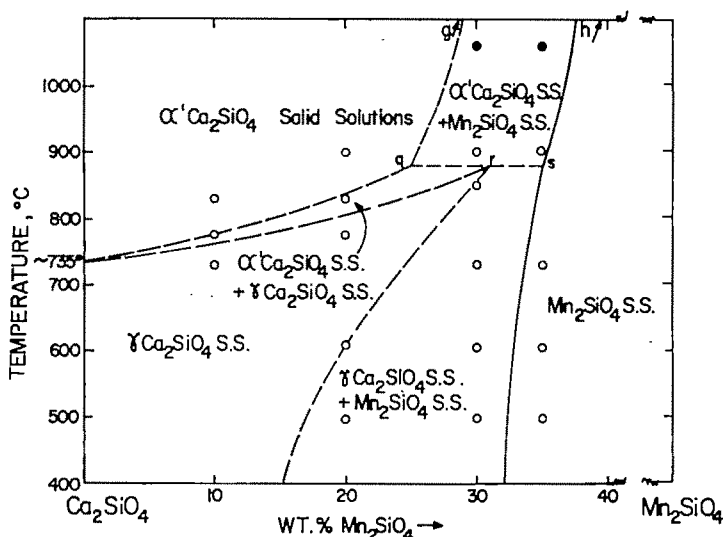


Fig. 4. Subsolidus relations between Ca_2SiO_4 and Mn_2SiO_4 . Dashed lines indicate approximate phase relations. Solid lines indicate the equilibrium relations are known more exactly. Individual runs are located by small open circles.

solid solutions and especially of the two phase region ($\alpha'\text{Ca}_2\text{SiO}_4$ solid solutions plus $\gamma\text{Ca}_2\text{SiO}_4$ solid solutions), separating the one-phase regions of homogeneous solid solution. Also, the maximum stability temperature of $\gamma\text{Ca}_2\text{SiO}_4$ solid solutions could not be determined accurately by quenching.

The limit of homogeneous tephroite-like olivine solid solutions can be determined with accuracy. At higher temperatures, the slope of this line and its intersection with the solidus is known. The slope of the line (extending downwards from h, fig. 1) may be followed experimentally to lower temperatures. Even small amounts of $\alpha'\text{Ca}_2\text{SiO}_4$ solid solution may be detected as a second phase in runs containing mainly tephroite solid solution. It can be recognized both microscopically and by dusting of the charges upon quenching. The other limit of the two-phase region (curve extending upwards from point q, fig. 4) may be located, although not with such accuracy, by examining quenched charges for the presence or absence of a tephroite-like olivine solid solution phase.

At lower temperatures, tephroite-like olivines come into equilibrium with $\gamma\text{Ca}_2\text{SiO}_4$ solid solutions. The equilibrium between these two solid solutions is less well established. Dry runs made in this temperature range fail to reach equilibrium, even allowing long periods of time (ca. 1 week). Results of hydrothermal runs are not generally applicable because of the stability of calcium silicate hydrates to high temperatures ($\sim 700^\circ\text{C}$) at the water vapor pressures used (2000-20,000 psi). Only at or above $\sim 700^\circ\text{C}$ are the results of hydrothermal runs applicable to determining the equilibrium between anhydrous phases. Hydrothermal runs made on appropriate compositions have yielded two olivine phases in equilibrium: ($\gamma\text{Ca}_2\text{SiO}_4$ solid solution + tephroite-like olivine) at or above 700°C . It is believed that these runs represent the equilibrium assemblage, and hence locate the position of the boundary curve extending through point s, figure 4.

A variety of starting materials including homogeneous, partially quenched, α' - Ca_2SiO_4 solid solution, and glasses containing some devitrified material plus some primary crystals (partially inverted α and α' - Ca_2SiO_4 solid solutions) have been used to determine the position of the curve extending through *h*s, figure 4, with concordant results. The 735°C figure for the α' - γ - Ca_2SiO_4 inversion is taken from Roy (1958). The position of the curves from the 735°C inversion to points *q* and *r* (fig. 4) has been located from the dusting of α' - Ca_2SiO_4 containing charges on quench and by analogy with the previously determined curves.

Results of dry and hydrothermal runs at subsolidus temperatures can be summarized as follows: at subsolidus temperatures a definite limit of homogeneous tephroite-glaucocroite solid solutions is reached. This limit lies between 30-40% Mn_2SiO_4 , at temperatures in the range 700°C-1200°C. Compositions between Ca_2SiO_4 and 30-40% Mn_2SiO_4 quench to yield one or more Ca_2SiO_4 solid solutions (α' , β , γ) or one or more of these solid solutions plus tephroite solid solution. Although the stability limits of the various Ca_2SiO_4 solid solutions have not been completely delineated, it is nevertheless clear that γ - Ca_2SiO_4 is not completely miscible with Mn_2SiO_4 .

Relation between the system Ca_2SiO_4 - Mn_2SiO_4 and related orthosilicate systems.—It is interesting to compare the results of the present study with those obtained in studies of related orthosilicate systems, e.g. Ca_2SiO_4 - Fe_2SiO_4 . Such comparisons help clarify the relation existing between ionic size, charge and polarizability, and the number and stability of compounds formed. These comparisons are particularly useful in extending the results of studies of such "simple" binary systems to cover the phase behavior of more complex orthosilicate phases, such as those encountered in crystallized slags, cements, or rocks.

Only one intermediate phase, CaMnSiO_4 , has been noted in this system. In this respect, the systems Ca_2SiO_4 - Mn_2SiO_4 and Ca_2SiO_4 - Fe_2SiO_4 are similar. The compounds CaMnSiO_4 and CaFeSiO_4 both form complete solid solutions with Mn_2SiO_4 and Fe_2SiO_4 respectively, and limited solid solutions with γ - Ca_2SiO_4 . The compound CaFeSiO_4 melts congruently at 1208°C (Bowen and others, 1935), while this study shows that CaMnSiO_4 may be regarded as incongruently melting. It appears therefore that the greater similarity of ionic size between Ca^{++} (1.06 Å) and Mn^{++} (0.91 Å), compared with the pair Ca^{++} and Fe^{++} (0.83 Å), tends to reduce the stability of the intermediate compound and increase the reciprocal solubility between the Ca_2SiO_4 modifications and Mn_2SiO_4 .

In another respect, however, the behavior of Mn^{++} resembles that of the much smaller Mg^{++} ion (0.78 Å). The range of incongruently melting compositions in this system is similar to that encountered in the system Ca_2SiO_4 - Mg_2SiO_4 . The crystalline phase resulting from the incongruent melting is a (Mg,Mn)O solid solution in the former case, and pure MgO in the latter.

SUMMARY

The system Ca_2SiO_4 - Mn_2SiO_4 is characterized by formation of a series of solid solutions based on Mn_2SiO_4 and the three stable polymorphic forms of

Ca_2SiO_4 . Although both $\gamma\text{Ca}_2\text{SiO}_4$ and Mn_2SiO_4 have the olivine structure, solid solution is not complete between $\gamma\text{Ca}_2\text{SiO}_4$ and Mn_2SiO_4 . The extensive series of olivine solid solutions based on Mn_2SiO_4 exhibits ordering at the 1:1 composition (CaMnSiO_4). This 1:1 composition exhibits the characteristics of a true compound except in its melting behavior. The solidus curve does not undergo any noticeable discontinuity on passing through this composition.

Liquidus relations are characterized by a pseudobinary minimum. The general slope of the liquidus profile, as well as the presence of a liquidus minimum are features common to other orthosilicate systems, e.g. $\text{Ca}_2\text{SiO}_4\text{--Fe}_2\text{SiO}_4$. However, compositions near the liquidus minimum in the $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$ system melt incongruently, producing $(\text{Ca,Mn})\text{O}$ solid solution.

The $\alpha'\text{Ca}_2\text{SiO}_4$ solid solutions can take considerable Mn_2SiO_4 into solid solution. Mn^{++} seems to have little, if any, action in inhibiting subsequent inversions. The large stability field of $\alpha'\text{Ca}_2\text{SiO}_4$ solid solutions at liquidus temperatures causes a wide range of compositions to dust even on rapid cooling.

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DIFFERENTIATION OF HAWAIIAN BASALTS: TRENDS OF MAUNA LOA AND KILAUEA HISTORIC MAGMA

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ABSTRACT. New analyses strengthen the conclusion that the historic lavas of Mauna Loa and Kilauea are derived from different magmatic batches. The presence or absence of hypersthene in the lavas seems to be related to the silica and lime contents.

In a recent paper dealing with the differentiation of Hawaiian basalts (Tilley, 1960), it was shown that the trend of Kilauean lavas could be separated from that of the historic flows of Mauna Loa as revealed in terms of iron/magnesium and alkali enrichment. The present contribution provides additional data relevant to this question strengthening the evidence that the historic lavas of Mauna Loa and Kilauea are derived from different magmatic batches (Powers, 1955).

The year 1868 is notable in the recorded history of Hawaiian volcano activity in that eruptions occurred almost simultaneously at Mauna Loa and Kilauea. In historic time no other simultaneous eruptions at the two centers are reported. There is a record of a summit eruption at Mauna Loa on March 27 of that year, but the main eruption occurred on April 7 along the southwest rift at an altitude of 3300 feet, breaking out 3½ miles above the Kahuku ranch. The flow, a picrite basalt, including a pahoehoe and aa phase, is reported to have lasted four days and eventually reached the sea. At Kilauea eruptions occurred on April 2 along the southwest rift of Kilauea in the Kau desert, SW of Maunaiki at an altitude of 2550 feet and also in the wall of Kilauea Iki (3350 feet) east of Kilauea Caldera. The lava at Kilauea Iki cascaded to the bottom of the crater and covered the entire floor. This 1868 lava has now been covered to a depth of 350 feet in the crater by the recent (November 1959) eruption (personal communication from K. J. Murata, Director of the Volcano Observatory at Hawaii). For representative material of these 1868 Kilauea eruptions we are much indebted to G. A. Macdonald of the University of Hawaii. The only chemical data on the Hawaiian 1868 eruptions are those provided by Washington, who supplied an analysis of the picrite basalt from the SW rift of Mauna Loa (Washington, 1923, p. 115-116). This picrite basalt flow has variants less rich in olivine, and one of us (C.E.T.) has collected an example from the flow near its east edge on Kahuku ranch.

Analytical data are now provided on this Mauna Loa variant and on three specimens of the 1868 flows of Kilauea (tables 2 and 1). The Mauna Loa picrite basalt shows conspicuous olivine, but clinopyroxene, hypersthene, and plagioclase are also developed as phenocryst minerals. Hypersthene in microphenocrysts may be jacketed by clinopyroxene. The analysis of the variant of the Mauna Loa eruption, poorer in olivine but containing the same phenocryst minerals as the picrite basalt, is given in table 2, no. 2. In table 3 some additional analyses of Mauna Loa lavas are provided: (a) three analyses of pre-

historic lava from the southwest rift all carrying olivine, hypersthene, clinopyroxene, and plagioclase as phenocrysts (table 3, 1-3) and (b) two historic lavas 1881 and 1887 (table 3, 5, 4) both of them hypersthene-bearing. Washington (1923) had previously supplied analyses of these two eruptions.

TABLE 1
Kilauea eruptions of 1868

			Norms		
1	2	3	1	2	3
SiO ₂	50.68	50.87	50.24		
Al ₂ O ₃	13.55	13.94	13.46		
Fe ₂ O ₃	1.39	1.85	1.17	Qz	1.20
FeO	9.35	9.07	10.94	Or	2.50
MgO	8.47	7.35	7.04	Ab	18.86
CaO	10.98	11.09	10.30	An	25.58
Na ₂ O	2.24	2.34	2.40	Di	21.88
K ₂ O	0.45	0.49	0.52	Hy	22.58
H ₂ O ⁺	0.09	0.15	0.30	Mt	2.09
H ₂ O ⁻	0.01	nil	0.11	Il	4.86
TiO ₂	2.54	2.86	2.92	Ap	0.67
P ₂ O ₅	0.26	0.25	0.17	Rest	0.10
MnO	0.17	0.17	0.18		
				100.32	100.20
	100.18	100.43	99.75		99.54

1. Olivine basalt (66128) 1868 flow of Kilauea, Kau Desert, 3 miles SW of Maunaiki, Hawaii.
2. Olivine basalt (66129) 1868 flow of Kilauea, center of floor of Kilauea Iki Crater, Hawaii.
3. Tachylite (66130) Spattercone, 1868 flow of Kilauea, foot of S wall of Kilauea Iki Crater, Hawaii. Refraction of tachylite glass 1.605.

TABLE 2
Mauna Loa eruptions of 1868

			Norms	
1	2		1	2
SiO ₂	49.27	51.03		
Al ₂ O ₃	9.38	13.20		
Fe ₂ O ₃	1.28	3.26	Qz	—
FeO	10.31	8.04	Or	2.22
MgO	17.74	9.40	Ab	15.20
CaO	7.46	10.02	An	16.40
Na ₂ O	1.80	2.22	Di	15.11
K ₂ O	0.42	0.42	Hy	27.24
H ₂ O ⁺	0.12	0.11	Ol	17.05
H ₂ O ⁻	0.06	0.01	Mt	1.86
TiO ₂	2.58	2.13	Il	4.86
P ₂ O ₅	0.26	0.24	Ap	0.67
MnO	0.09	0.17	H ₂ O [±]	0.18
	100.77	100.25	100.79	100.17

1. Picrite basalt (hypersthene), lava of 1868, SW rift of Mauna Loa (Washington, 1923, p. 115).
2. Hypersthene basalt (64/66084), lava of 1868, road near E edge of flow in Kahuku Ranch, Hawaii.

1868 ERUPTIONS OF KILAUEA

Three analyses of the rocks of the 1868 Kilauea eruptions are set down in table 1, 1-3. The first analysis is that of the flow from the Kau desert, a vesicular basalt carrying phenocrysts of olivine, clinopyroxene, and plagioclase, sometimes collected together in glomeroporphyritic aggregates. The lava from the center of the floor of Kilauea Iki crater (table 1, no. 2) is finer grained with a feathery base but carrying olivine phenocrysts and less conspicuously porphyritic clinopyroxene and plagioclase. A spatter cone at the foot of the south wall of Kilauea Iki crater provides a tachylyte (table 1, no. 3) in the form of a light brown glass as seen in thin section, refraction 1.605, and holding a few phenocrysts of olivine with smaller crystals of plagioclase and a little acicular clinopyroxene. The positions of the new analyses provided in this communication are plotted in the diagrams of figures 1 and 2 relating iron enrichment/silica and alkalis/silica. As developed in the paper already referred to (Tilley, 1960), the Kilauean trend is portrayed in the line joining the analyzed variants of the 1840 Puna eruptions. The Mauna Loa trend is here presented in the join of the two analyses of the 1868 picrite basalt and basalt (table 2, 1-2). These indicated trend lines lie somewhat to the left of the weighted averages of Mauna Loa and Kilauea historic magma (shown as L and K in the figures).

It is of interest to observe the relative positions of the three Kilauean lavas of 1868 to those of the 1868 Mauna Loa series. The tachylyte of Kilauea Iki lies on the Kilauea line in both plots, the vesicular basalt from this locality close to a 1920 Kilauea flow with the Kau desert lava, a little further removed. The group position of the 1868 Kilauea basalts is that associated with the Kilauea trend and distinct from the Mauna Loa trend in both figures. There is, however, an important petrographic as well as chemical distinction between the two groups of eruptions. The Mauna Loa eruptions carry hypersthene, the Kilauean do not, a distinction which merits further consideration. Macdonald (1949) long ago noted that hypersthene phenocrysts were fairly common in the historic basalts of Mauna Loa but very rare in the lavas of Kilauea. In the hypersthene-bearing lavas hypersthene and a clinopyroxene usually occur together as microphenocrysts, the former frequently being jacketed by a layer of clinopyroxene. Clearly in the complex Mauna Loa liquid from which these pyroxene phases were crystallizing simultaneously, the solidus of the system cut in projection the pyroxene solvus (cf. Boyd and Schairer, 1957, for the behavior of the artificial system $\text{MgSiO}_3\text{—CaMgSi}_2\text{O}_6$).

The historic Mauna Loa lavas are as a batch higher in silica and lower in lime than the Kilauea batch. In lavas of the same silicity the Mauna Loa type is also lower in alkalis. It is significant that the few Kilauean lavas that carry hypersthene are the more siliceous types, lower in lime. Examples are the lava of the upper vents of the 1840 eruption (1840_b) and the more siliceous of the 1955 suite in east Puna (82). Among prehistoric Kilauean assemblages, hypersthene and augite are found together in the metamorphosed picrite basalts (Muir and Tilley, 1957) and in the Uwekahuna gabbro of the Kilauean Caldera (U of figs. 1 and 2). The picrite basalts have, however, been recrystal-

TABLE 3
Lavas of Mauna Loa

	1	2	3	4	5	Norms				
						1	2	3	4	5
SiO ₂	49.45	50.19	50.35	51.77	51.96	—	0.65	—	1.98	3.24
Al ₂ O ₃	11.77	12.53	12.21	13.78	13.65	Qz	1.67	2.78	2.22	1.95
Fe ₂ O ₃	2.70	3.52	2.76	2.04	1.67	Or	16.77	18.08	19.91	19.39
FeO	8.60	7.76	8.55	9.13	9.38	Ab	22.36	22.38	25.85	25.85
MgO	13.84	11.47	11.58	8.58	8.01	An	17.22	16.82	18.97	19.69
CaO	9.02	9.66	9.03	10.12	10.24	Di	26.25	30.87	24.58	23.14
Na ₂ O	1.98	2.10	2.16	2.36	2.28	Hy	7.65	—	—	—
K ₂ O	0.29	0.31	0.50	0.39	0.36	Ol	3.65	4.10	3.34	3.95
H ₂ O ⁺	0.24	0.25	0.26	0.07	0.09	Il	3.94	4.06	3.02	2.44
H ₂ O ⁻	0.06	0.04	nil	0.06	nil	Mt	0.34	0.67	0.34	0.34
TiO ₂	1.90	2.10	2.14	1.76	2.11	Ap	0.30	0.26	0.13	0.09
P ₂ O ₅	0.19	0.20	0.29	0.17	0.16	H ₂ O [±]	100.15	100.02	100.34	100.08
MnO	0.16	0.16	0.17	0.16	0.17					
	100.20	100.29	100.00	100.39	100.08					

1. Hypersthene basalt (62/66082), pahoe-hoe phase, prehistoric lava, Kahuku Series, Kahuku Pali, trail to S point (Kalaie), Hawaii.
2. Hypersthene basalt (63/66083), aa phase, prehistoric lava, Kahuku Series, Kahuku Pali, trail to S point (Kalaie), Hawaii.
3. Hypersthene basalt (61/66081), prehistoric lava, Kau Series, 3.3 miles NNE of Honuapo, Hawaii.
4. Hypersthene basalt (57374), lava of 1887, highway crossing flow on the SW rift, Hawaii.
5. Hypersthene basalt (60/66080), lava of 1881, 1 mile below Kamana village, W of Hilo, Hawaii.

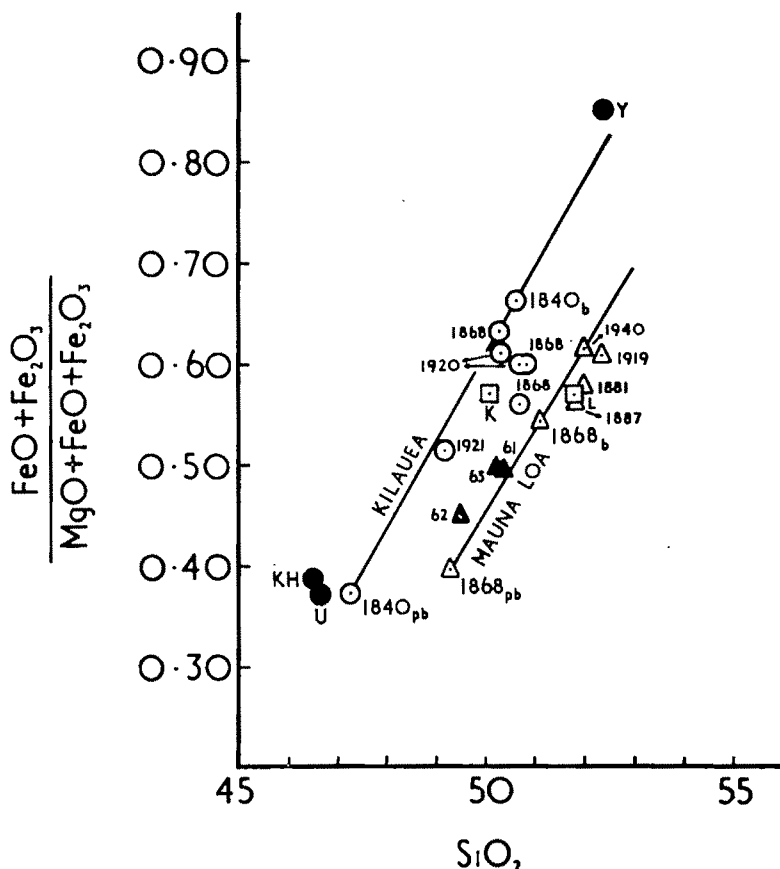


Fig. 1. Plot of analyses of Hawaiian lavas (iron enrichment/silica) showing the grouping of Kilauean and Mauna Loa flows and the position of the 1868 flows of each volcano (tables 1 and 2). Historic flows with indicated dates, Kilauea, open circles; Mauna Loa, open triangles. Prehistoric flows, filled circles; Mauna Loa, filled triangles. U gabbro, KH picritic basalt, Kilauea (Washington, 1923, table 2, analyses 1 and 2), Y iron-rich tholeiite segregation vein in basalt (Kuno, 1957, p. 188). 61, 62, 63 prehistoric flows of Mauna Loa (table 3, analyses 3, 1, 2). New analyses of the historic flows of Mauna Loa (1881 and 1887) are plotted in the diagram (table 3, analyses 5 and 4). K weighted average Kilauean historic lava; L weighted average Mauna Loa historic lava (Powers, 1955, p. 88). Other dated flows (Macdonald, 1949, U. S. Geol. Survey Prof. Paper 214D, analyses p. 63 and 74).

lized in the solid, and the occurrence of hypersthene in this environment denotes a development in the subsolvus region of the pyroxene solid solution. The gabbro (U) occurs as a sill in the wall of the Caldera, and it is reasonable to conclude that it crystallized under subvolcanic conditions with retention of water, thus promoting the crystallization of the orthorhombic pyroxene at lower temperatures than prevailed in the crystallization of the surface lavas of picrite basalt composition (such as 1840_{pb}).

It has been noted that broadly the Mauna Loa lava series is distinguished by higher silicity and lower lime content compared to the Kilauean series. If

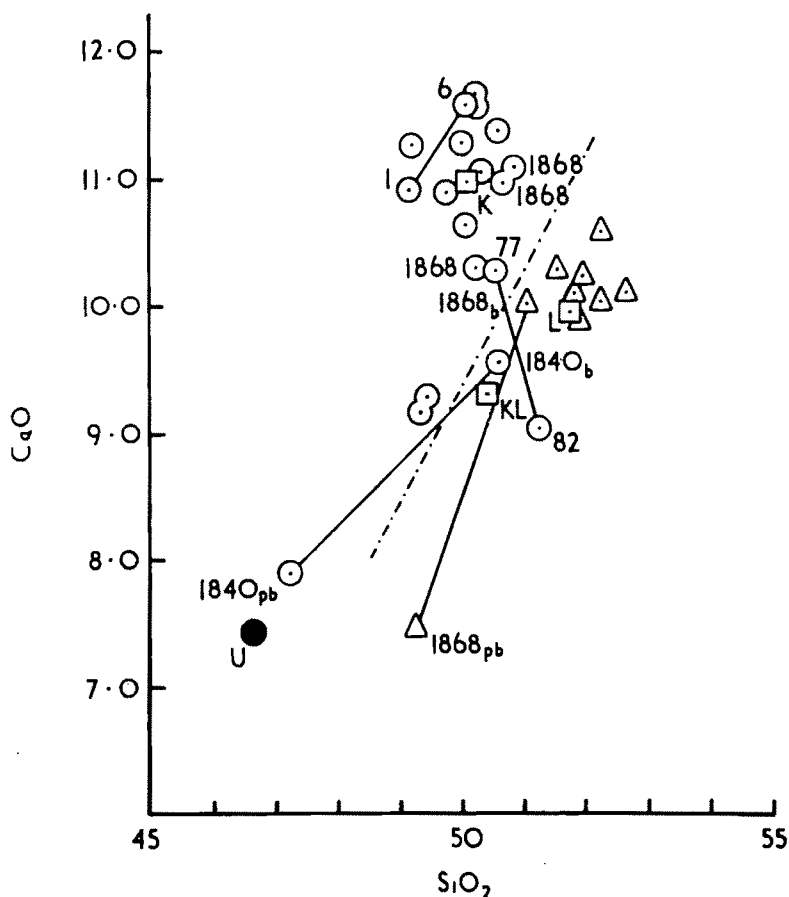


Fig. 3. Plot of analyses of Hawaiian lavas (lime/silica) showing the grouping of historic flows of Kilauea (circles) and Mauna Loa (triangles). Numbers as in figures 1 and 2 with the addition of 1-6, Kilauea series of 1921 (Tilley, 1960, table 1); 77-82, Kilauea series of 1955 (Tilley, 1960, table 4). KL average of 7 analyses of basalts of Koolau series, Oahu (table 4). The broken line in the figure separates the field of hypersthene bearing lavas (below) from the field of lavas without hypersthene (above).

The plot reveals that the Koolau basalts straddle the positions of the Mauna Loa and Kilauea series, both as regards their iron/magnesium ratios and their alkali content, though the subsidiary trend shown (9-2) follows the Mauna Loa trend of figures 1 and 2. As a group the Koolau series are conspicuously hypersthene-bearing, this mineral appearing as phenocrysts though occasionally it is restricted to the groundmass. A new average of the Koolau basalts is given in table 4 together with a new analysis of a tachylite of the

series from the Pali. This average (KL) plots in the hypersthene field of figure 3 as do the majority of the analyzed members. It is clear that the position now reached in the study of Hawaiian tholeiitic basalts calls for continued investigation and notably for an extended chemical and petrographic examination of the prehistoric lavas of Mauna Loa and Kilauea in an attempt to unravel the earlier magmatic evolution of these two volcanoes.

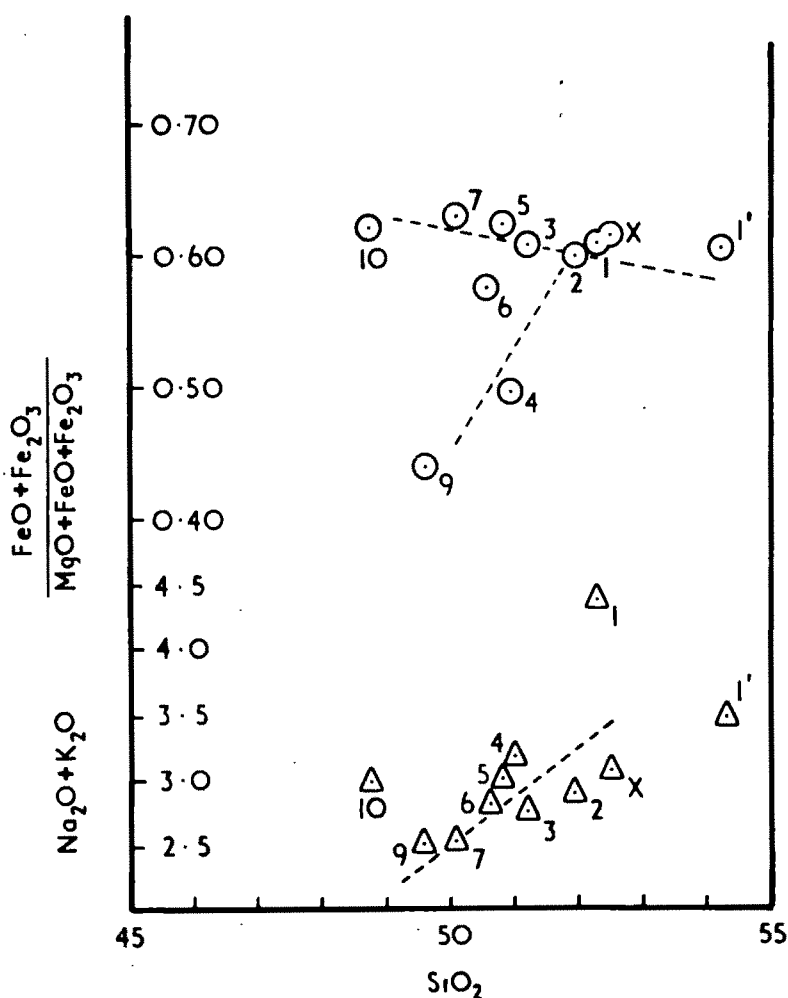


Fig. 4. Plot of analyses of lavas of Koolau Series of Oahu (iron enrichment/silica, alkalis/silica). Numbers refer to analyses 1-10 of table 4 of Wentworth and Winchell (1947, p. 71) with additional points 1', Palolo dike, Honolulu (Tilley, 1960, p. 41), X Tachylyte selvage to dike, Pali, Oahu (new analysis, this paper table 4, no. 1).

TABLE 4
Koolau basalts, Oahu

	1	2	Norms	
			1	2
SiO ₂	52.53	50.39		
Al ₂ O ₃	13.69	14.59		
Fe ₂ O ₃	2.53	3.03	Qz	5.58
FeO	8.65	7.86	Or	2.78
MnO	0.16	0.09	Ab	20.96
MgO	6.95	8.49	An	24.74
CaO	9.66	9.32	Di	18.08
Na ₂ O	2.50	2.56	Hy	19.29
K ₂ O	0.55	0.27	Mt	3.71
H ₂ O ⁺	0.48	0.68	Il	3.80
H ₂ O ⁻	0.29	0.26	Ap	0.34
TiO ₂	2.04	2.21	Rest	0.77
P ₂ O ₅	0.21	0.19		
	100.24	99.94	100.05	99.90

1. Tachylyte, selvage of dike, Pali, Oahu. Refraction of glass 1.587, sp.gr. 2.77.
2. Average of 7 analyses of Koolau basalts, Oahu.

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A POLLEN DIAGRAM FROM SOUTHEASTERN CONNECTICUT

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California

and

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ABSTRACT. A pollen diagram has been constructed from cores taken from the Red Maple Swamp in the Connecticut Arboretum Natural Area at Connecticut College, New London. The pollen diagram shows a zone of much spruce-pine pollen and high N A P at the lower level followed by a zone dominated by spruce with two spruce maxima. This is followed by a zone dominated by pine and then by a zone dominated by deciduous tree pollen. The lowest zone, T-2, suggests a spruce-pine park-tundra type vegetation followed by the T-3 zone, where N A P is most abundant, indicating a dominance of herbaceous and shrubby forms. This latter zone (T-3) represents a most severe climatic interval which is presumed to correlate with the temporary halt of the ice three miles north of the Red Maple Swamp (Ledyard moraine). Within the spruce period, two spruce maxima are separated by a minimum which represents a time of climatic amelioration correlated with the Two Creeks Interval. The second spruce maximum is correlated with the Valdres advance. Well-differentiated stages within the C-zone, typical of most inland diagrams, are lacking. This is probably due to the coastal position of the Swamp.

INTRODUCTION

A number of Connecticut bogs and lakes have been studied palynologically by Deevey (1939, 1943) and Leopold (1955, 1956). The purpose of this paper is to add to our present knowledge of the postglacial history of southeastern Connecticut and to correlate the findings with those of other investigators.

This study is part of a series of bioecological projects being conducted in the Connecticut Arboretum. The field work was done by the senior author as an undergraduate study aimed at determining certain aspects of the past vegetational history of the natural area. The pollen analysis here reported is one part of this study (Beetham, 1956 unpub.).

The pollen profile was obtained from the Red Maple Swamp in the Connecticut Arboretum Natural Area west of the Connecticut College campus. A road, Gallows Lane, crosses the area in the Town of Waterford (exact location Uncasville Quadrangle, southwest sector 41° 21' 50" N, 72° 06' 55" W). The Arboretum lies within the central hardwoods-hemlock zone (Westveld and others, 1956), in which oaks are the characteristic species. The uplands surrounding the Red Maple Swamp are covered by a young oak-hemlock-birch forest (Niering, 1956). The swamp supports a second growth forest of red maple (*Acer rubrum*) with a dense shrub layer of highbush blueberry (*Vaccinium corymbosum*) and sweet pepperbush (*Clethra alnifolia*). Species such as leatherleaf (*Chamaedaphne calyculata*) and water-willow (*Decodon verticillatus*), which were probably more widespread in the past, still persist in scattered openings.

METHODS

The samples were first taken from the swamp at 6" intervals with the Davis peat sampler. These samples were prepared for analysis by the KOH method, and 150 grains of pollen were counted at all except the lowest levels.

The pollen profile constructed from analysis of the first samples was of sufficient interest to warrant removal of larger samples for radiocarbon dating and more precise analysis of the lower levels. A 2-in. Livingstone borer was then used to provide a continuous core. From this core, samples for radiocarbon dating were taken from the 4.0- to 4.1-m and 5.2- to 5.3-m levels. Samples were also removed at 10-cm intervals for more detailed analysis. In two places part of the core was discontinuous, but only small amounts of material were lost.

To free more of the pollen from the lower levels, samples were prepared for analysis by the bromoform-acetolysis method; 150 grains including arboreal and nonarboreal pollen were counted at each level.

RESULTS

Sediments.—Sediments were collected to a depth of 6.7 m, below which it was impossible to lower the sampler. At the lowest level (6.7 to 5.7 m), the deposits consisted of grayish-tan silt with tiny particles of mica and flecks of blueish material. At about 5.7 m the silt gave way to a smooth black gyttja and above this (3.5 to 1.0 m) to a fibrous peat. Within the fibrous peat layer two different textural types were encountered—a coarse blackish material (3.5 to 1.5 m) underlying a finer dark brown peat (1.5 to 1.0 m). Above this layer a dark-black forest peat extended to the surface.

Pollen profile.—The pollen diagram from the Red Maple Swamp (fig. 1) reveals pollen zones closely resembling those reported for other localities in the northeastern United States (Deevey, 1939, 1943; Leopold, 1955, 1956; Davis, 1958; Ogden, 1959; Krauss and Kent, 1944). The characteristics of the zones recognized at the Red Maple Swamp are summarized and related to those from southern New England in table 1. At the lowest levels is a zone (T) with abundant nonarboreal pollen. At successively higher levels is a zone (A) dominated by spruce pollen followed by zone B, rich in pine pollen, above which is a zone dominated by pollen of deciduous trees.

Within the T zone two subzones are distinguishable: the T-2 at the lowest levels, where tree pollen reaches 50-75 percent; and above this the T-3, where tree pollen decreases and the nonarboreal pollen reaches a peak. In the T-3 subzone the most abundant families of nonarboreal pollen are, in order of importance, the Compositae, Cyperaceae, Gramineae, and Ericaceae. Of the herbs, pollen of the Ambrosiaceae was most abundant and accounted for the highest peaks. As the silt is succeeded by gyttja, the T-3 zone is succeeded by the A-zone characterized by abundant spruce pollen. In this zone two spruce maxima are located at the 5.0-m level (A-2) and the 4.1-m level (A-4). At the 4.0- to 4.1-m level within the A-4 a radiocarbon date of $10,480 \pm 140$ years (Y-447E) has been established, and an older date has been recorded for the 5.2- to 5.3-m level in the A-1 at $13,290 \pm 120$ years (Y-447D). (Barendsen, Deevey, and Gralenski, 1957). The sharp dip in the profile for spruce pollen at 5.2 m (A-1)

TABLE 1

Red Maple Swamp sequence compared with other Southern New England studies (Leopold, 1955). Radiocarbon dates are averages taken in part from Deevey (1958) and are all Connecticut samples except A-3 which is from Athol, Massachusetts.

SOUTHERN NEW ENGLAND			RED MAPLE SWAMP		
Zone	Vegetation	Age B. P.	Glacial Substage and Climate	Vegetation	Age B. P.
C-3b	Spruce, pine increasing		Moister and possibly	{ Oak-birch- hemlock- chestnut	
C-3a	Oak-hemlock	1970	cooler		
C-2	Oak-hickory	5230	Warm, dry		
C-1	Oak-hemlock		Warm, moist	Oak-hemlock	
B	Pine	8020	Warmer and drier	Pine	
A-4	Spruce	10,460	Cold-Valders	Spruce	10,480
A-3	Pine-spruce-oak	10,800	Cool-Two Creeks	Spruce-pine	
A-2	Spruce-birch	12,780	Cold	Spruce-birch	
A-1	Spruce increasing		Cold	Spruce increasing	13,290
T-3	High N A P-pine	*12,800	Middletown readvance or Ledyard moraine	{ High N A P, Spruce- pine minimum	
T-2	Spruce	*13,500	Cold	N A P, Spruce-pine increases	
T-1	High N A P-pine		Very cold		

*Only one radiocarbon date available.

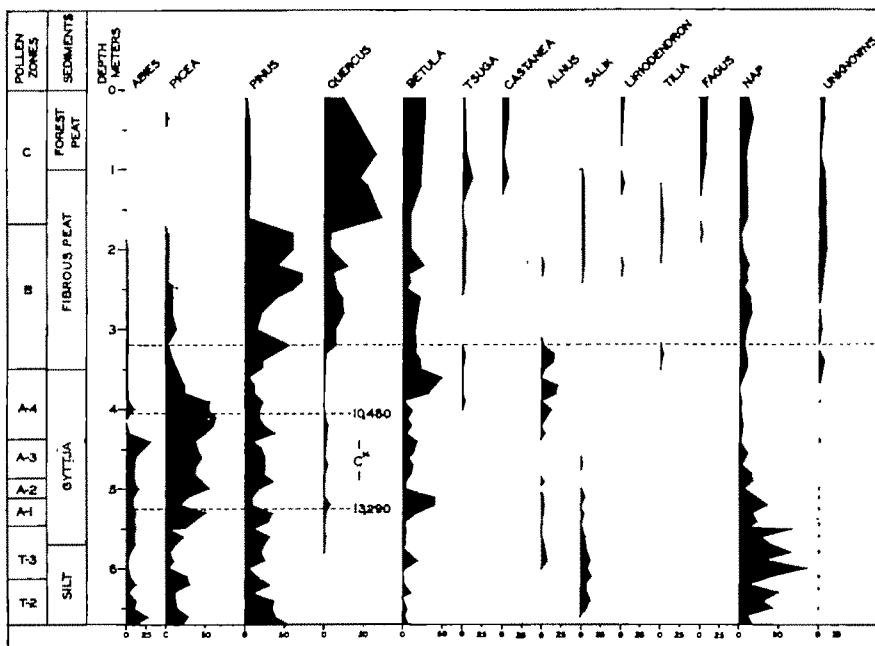


Fig. 1. Pollen diagram of the Red Maple Swamp, Connecticut Arboretum Natural Area at Connecticut College. Diagram is a composite of two samplings. Section above broken line at 3.2 m was derived from initial samples, whereas that below was obtained as a result of more detailed studies from a continuous core.

may reflect a local catastrophic event such as fire, which could account for the temporary rise in abundance of birch pollen shown in the diagram at this point. The zone dominated by spruce gives way to a zone dominated by pine, and this is ultimately succeeded by a zone dominated by deciduous tree pollen.

INTERPRETATION OF PROFILE

The results closely parallel the recent findings of Leopold (1955, 1956) in Connecticut and Davis (1958) in central Massachusetts, which show a zone (A) containing two spruce maxima preceded by a zone (T) where nonarboreal pollen predominates. The lowest subzone (T-2) suggests a spruce-pine park-tundra vegetation where tree growth was able to become rather well established for a limited time. However, this interval is followed by the T-3 zone, where presumably the previous milder climate deteriorated, thus favoring shrub and herbaceous cover and limiting tree growth. In Connecticut the N A P peak (T-3) has been correlated with the Middletown readvance. In this study an N A P peak found in a similar position in the sequence may also be correlated. However, a more local halt in the retreat of the ice (Ledyard moraine) has recently been reported three miles north of the Red Maple Swamp (Goldsmith, written communication). With these new data one would be inclined to correlate T-3 in this study with the more local phenomenon, but it is possible that the correlation should be with the Middletown advance and the pollen zone

equivalent to the Ledyard pause would occur at a lower level. This zone is also correlated with the Port Huron moraine in Lake Michigan and the Mankato maximum to the south of Lake Superior (Wright and Rubin, 1956). At Totoket Bog, Connecticut, the T-2 zone has been dated (Deevey, Grahenski, and Hoffren, 1959) at $13,280 \pm 420$ years (Y-502) and the T-3 at $12,350 \pm 400$ years (Y-505). At Totoket, approximately 50 miles to the west, Leopold (1955, 1956) found one lower subzone (T-1) containing a high N A P count. The apparent absence of this subzone may warrant further investigation.

As climatic conditions ameliorated in the period represented by zone A-1, spruce increased and rose to a maximum in the period represented by A-2. Climatic conditions were cold but not severe enough to prevent the establishment of spruce as a more continuous vegetation type. The radiocarbon date of 13,290 years estimated for the A-1, when compared to other dates, falls between the average of 12,780 years for the overlying A-2 and the underlying T-2 of 13,500 years.

In A-3 spruce pollen decreases somewhat and pine rises, which indicates a period of further climatic amelioration that appears to correlate with the Two Creeks Interval dated at 11,400. The return to a second spruce maximum in A-4 would suggest a period of some climatic deterioration that is presumably correlated with the time of Valders advance. The radiocarbon date $10,480 \pm 140$ years (Y-447E) (Barendsen, Deevey, and Grahenski, 1957) from A-4 agrees closely with the 1957 measurement Y-504 from Totoket set at $10,440 \pm 200$ years (Deevey, Grahenski, and Hoffren, 1959), with the average for A-4 at around 10,460 years.

The transition to the zone dominated by pine indicates a change to a period with a drier and possibly warmer climate, probably favorable for several species of pine. In central Massachusetts Davis (1958) notes that size frequency studies would suggest that jack and red pine, species of a northern affinity, dominated during the early part of the period followed by white and pitch pine as the climate continued to ameliorate. Although the age of the pine period was not determined here, the C^{14} date (C-39) of 8320 years (Deevey, 1958) from zone B, Upper Linsley Pond, some 45 miles to the west, may not be an unreasonable figure for the pine period represented in the Red Maple Swamp.

Within the zone dominated by deciduous tree pollen the various subzones described by other investigators are not clearly delineated in the Red Maple Swamp profile. The oak-hemlock maximum (C-1) following the pine maximum (B) may be present at the 1.1-m level where hemlock is most numerically important. In general the C zone resembles the zone containing the hemlock-birch-oak-chestnut maximum (C-3) of Davis' (1958) diagrams from central Massachusetts. The sediments are also similar in that the fibrous peat, presumably laid down under drier conditions (pine period), is overlain by a finer-textured material, possibly indicative of a moister climate at the beginning of the period dominated by deciduous trees. Davis mentions that this superposition marks the reoccurrence of bog development in northwestern Europe at the beginning

of Sub-Atlantic time, which has been archaeologically dated at 600 B.C. (Granlund, 1932). Bog development may have occurred in the northeastern part of this continent at about the same time (Davis, 1958, p. 567), ending the Hypsithermal interval when prevailing temperatures were presumably higher than today (Deevey and Flint, 1957). Because hickory was not found in the profile the typical oak-hickory association (C-2 zone), widely reported as typical of this period, is absent. Its absence here, but presence in a nearby shallow bog 1200 feet to the south is of considerable interest. Here, throughout the sediments, which are only 1 meter in depth, hickory pollen is present at all levels sampled. The other species present, in order of importance, include oak, birch, chestnut, maple, hemlock, and beech. The absence of hickory pollen in the Red Maple Swamp may indicate that the pre-existing bog closed before hickory as a component of the upland vegetation moved into southeastern Connecticut. Radiocarbon dates of peat from the upper levels of the Red Maple Swamp and the nearby bog would aid in clarifying this question. The small amount of spruce pollen near the top of the Red Maple Swamp suggests that probably black spruce was present when the swamp finally closed and therefore grew in southeastern Connecticut in relatively recent time. It is not growing in the area at the present time. Possibly competition from deciduous species such as red maple along with a warming climate eliminated the spruce.

The abrupt increase in birch pollen as the Red Maple Swamp closed may indicate a local disturbance, such as fire or hurricane, which opened the forest canopy sufficiently to bring about a temporary dominance of birch. In fact, even today birch, especially black birch, is abundant throughout the surrounding upland, partly because of the abundance of ledges favoring its establishment and partly because occasional hurricanes create openings for it.

The somewhat anomalous pollen assemblages of the C zone in the Red Maple Swamp may well be due to the coastal location of the swamp. The nearness of the ocean may have modified the regional climatic conditions during the period represented by this zone so that the pronounced changes in the pollen assemblages further inland are not recognized here.

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DISCUSSION

THE CONTROL OF ANORTHITE CONTENT OF PLAGIOCLASE IN METAMORPHIC CRYSTALLIZATION

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The paper by de Waard (this JOURNAL, October 1959) provides very valuable field evidence for the view (Fyfe, Turner, and Verhoogen, 1958, p. 218) that in regional metamorphism the transition from An_5 to An_{20} in plagioclase associated with epidote takes place over a very narrow temperature pressure field.¹ De Waard's application of his results to the facies classification is, however, open to question. He suggests that the abrupt change in plagioclase composition is coupled to the formation of garnet in pelites and of hornblende in basic rocks, and he accepts the An_{10} isopleth as the upper boundary of the Greenschist Facies. This view can hardly be discounted, but it will be remembered that assemblages containing garnet or hornblende in equilibrium with albite are not uncommon (Epidote-Amphibolite Facies of Vogt (1927); Quartz-albite-epidote-almandine subfacies of Fyfe, Turner, and Verhoogen (1958)). Thus the development of these minerals has not always brought about a change of plagioclase composition, and de Waard's suggestion is inadequate. He also objects, on the basis of his frequency curves (figs. 4 and 5, p. 558-559), to the arbitrary nature of the An_{20} isopleth as a facies boundary. The present writer would therefore like to draw attention to a factor which may be of critical importance in considering both the An_{10} and An_{20} isopleths as facies boundaries, i.e. the varying stability of the plagioclases in the low temperature structural state.

The simple lamellar twinning or absence of twinning found in the metamorphic schists contrasts strongly with the variety of twinning found in igneous rocks (Phillips, 1930; Gorai, 1951; Turner, 1951). It now seems likely that much of this twinning is secondary and has been produced through structural transformations in the feldspars with falling temperature. Its paucity in the metamorphic schists therefore strongly suggests that the feldspars there have originally grown in the low temperature structural state, and the evidence of such twinning as is present may be quite compatible with this view (Smith, 1958). The experimental evidence on the ordering of albite (MacKenzie, 1957) also shows that relatively ordered forms are to be expected at metamorphic temperatures.

Thus we may infer that in regional metamorphism under conditions of high hydrostatic and distortional stress the plagioclase feldspar that grows in equilibrium with epidote is in the low-temperature structural state. It seems significant, therefore, that the most important structural changes with com-

¹ The determinative method used (Turner, 1947) can be ambiguous in the range under discussion, and the results could be accepted with greater confidence if they had been checked by refractive index and optical axial angle determinations with reference to the most recent curves (Smith, 1956, 1957). However, it is likely that the results are not significantly in error.

position in the low temperature feldspars take place at just those compositions which de Waard has discussed, that is, at approximately An_5 , An_{20} , and An_{30-35} .

Laves (1954) has shown that the low-temperature plagioclases in the range An_5 - An_{17} show submicroscopic unmixing of An_5 and An_{30} fractions to produce the peristerite structure. This work demonstrates that there must be a solvus curve below which sodic oligoclase is unstable; and even above the solvus we may expect that sodic oligoclase will be relatively less stable than albite or calcic oligoclase. In other words, where, in the crystallization of a metamorphic rock, plagioclase grows in the low temperature state and has to compete for its calcium content with epidote, we may expect that sodic oligoclase will be stable over a relatively narrow temperature-pressure field; and thus a rapid transition from albite to calcic oligoclase may be characteristic of synkinematic metamorphism. By this hypothesis, the transition could still take place at the same time as the development of garnet or hornblende but it would not necessarily be tied to these changes. Further, the An_5 isopleth may be regarded as a more natural facies boundary than the An_{10} isopleth.

However, the recognition of the An_{10} or An_5 isopleth as a valuable facies boundary should not preclude the recognition of a separate facies in which oligoclase is in equilibrium with epidote (Saussurite Facies (Rosenqvist, 1952); Floitite Facies (Becke, 1921)). Such a facies is also valuable provided that its upper boundary makes a useful division of the PT field between the top of the Greenschist Facies and the top of the Amphibolite Facies.

The theoretical equilibrium curve for the epidote-plagioclase relation (Ramberg, 1949) shows epidote in equilibrium with even the most basic plagioclase, but above about An_{30} the curve flattens so that the more basic plagioclase is in equilibrium with epidote over a relatively narrow PT field. Epidote will generally not persist through this field to its upper stability limit, owing to shortage of calcium; and the upper stability limit of epidote will not be well defined even for known pressure conditions because of the effect of solid solution of Fe^{2+} and Mn^{2+} (Rosenqvist, 1952; Miyashiro and Seki, 1958). The selection of the An_{30} isopleth by Ramberg (1949, p. 25) to define an upper limit to the Saussurite Facies, corresponding roughly to the lower stability limit of diopside pyroxene, therefore seems reasonable. It does not encroach too far on the amphibolite facies, and rocks with the association oligoclase-epidote are widely distributed in regional metamorphism (Kvale, 1946). It also appears to agree approximately with the upper stability limit of the albite-zoisite assemblage (Kennedy, 1949) and with the upper limit of the staurolite zone in pelites (Francis, 1956). It may now be added, in view of de Waard's objection, that the An_{30-35} composition range is not arbitrary from the point of view of the structures of the low temperature feldspars, and, indeed, de Waard's frequency curves show a marked steepening above An_{35} . It has long been recognized that above about An_{30} the structure of the plagioclase feldspars can be interpreted in terms of unit cell stacking of the albite and anorthite structures (Chao and Taylor, 1940; Tuttle and Bowen, 1950; Cole, Sörum, and Taylor, 1951). This intermediate feldspar structure apparently extends down to An_{23} (Gay and Smith, 1955) but De Vore (1956) has pointed

out that, apart from pure anorthite, plagioclase of composition $An_{53.3}$ is the only plagioclase feldspar that can have only one kind of Si and Al in its structure. It is an easily ordered low energy structure which is favored when exsolution proceeds in the composition range on either side. It seems very likely, therefore, that the structural changes in this range will have great importance in the subsolidus plagioclase-epidote equilibrium. They may well bring about a sudden increase in the acceptability of calcium in feldspar at the expense of epidote and help to account for the disappearance of the latter. Conversely, the presence of epidote in regionally metamorphosed rocks can be ascribed in part to the relative instability of the low temperature feldspars in the range An_8 - An_{30-35} . The selection of the An_{30} , or better the An_{35} , isopleth to define the upper boundary of the Saussurite Facies therefore receives important justification, provided that the plagioclase-epidote association can be recognized as a true equilibrium relationship.

De Waard has not discussed this association in detail, and it is therefore difficult to be sure whether he is dealing with a true equilibrium relationship. His reported occurrence of labradorite or bytownite with epidote (1959, p. 554) and the occurrence of reversed or oscillatory zoning (p. 555) may indicate that some of the plagioclase is of relict igneous origin. The present writer (1958) has found oscillatory zones of bytownitic composition in relict plagioclases of basic schists where the regional metamorphism has produced andesine. Further, the epidote in these rocks does not appear to have been developed in the synkinematic metamorphism but is a postkinematic product associated with the granitization of the rocks. Thus the plagioclases often show a gradational zoning due to metasomatism, and the epidote is in equilibrium with the most sodic plagioclase. It does not seem that this last factor can have been important in the rocks described by de Waard unless the epidote belongs to his phase of retrogressive phyllonitization, but he does recognize the occurrence of normal gradational zoning (1959, p. 555).

If these hazards are recognized, it appears to the writer that the An_{35} (or An_{30}) isopleth taken in conjunction with the disappearance of epidote remains a useful facies boundary of similar status to the An_8 (or An_{10}) isopleth. Both isopleths mark important structural changes in the low temperature feldspars so that the plagioclase-epidote equilibrium curve may be expected to show abrupt changes of slope at these compositions; and thus de Waard's empirically derived curves showing the relation of plagioclase composition to grade of metamorphism can be regarded as better approximations to a plagioclase-epidote equilibrium curve than Ramberg's (1949) diagram. Clearly, however, under different conditions of metamorphism (e.g. normal contact metamorphism), where the plagioclase may crystallize in a higher temperature structural state, the form of the curve may be different.

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ERRATUM

COMPOSITIONAL CHARACTERISTICS AND EQUILIBRIUM RELATIONS IN
MINERAL ASSEMBLAGES OF A METAMORPHOSED IRON FORMATION

ROBERT F. MUELLER

Certain values in table 1, p. 457 of the above-mentioned paper which appeared in this Journal (v. 258, p. 449-497) are transposed. The corrected table is as follows:

	DH11- 200	10G	DH13- 607	DH7- 291
FeO	5.5	5.8	6.0	4.1
MnO	0.38	0.25	0.48	0.39
MgO	22.0	22.0	21.0	23.0
CaO	11.5	11.0	12.5	12.5
Na ₂ O	nd	0.58	nd	nd
K ₂ O	nd	0.07	nd	nd

The following additional corrections should also be made:

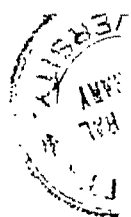
On p. 469 (table 4) for Mn(Mg + Fe + Mn) of Ca-pyroxene of specimen 12BA read 0.0106 rather than 0.0160.

On p. 493 make the following changes: In reaction (s) read $4/3 \text{ SiO}_2$ rather than $1/3 \text{ SiO}_2$. In equation (21) read ΔG_o° rather than ΔG_s° ; and in the equation following the words "division of equation (19) by equation (21) gives" read $(P'_{\text{O}_2})^{-1/4}$ rather than $(P'_{\text{O}_2})^{1/4}$.

These corrections do not affect the rest of the paper.

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THE FLOOR OF CRATER LAKE, OREGON

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ABSTRACT. Soundings recently made of the floor of Crater Lake by the U. S. Coast and Geodetic Survey show a maximum depth of 1932 feet. They reveal the presence of a submerged cone, one mile across at the base and approximately 1320 feet high, from which flows spread southeastward to form an extensive lava plain. The soundings also reveal a submerged field of lava extending two miles eastward from Wizard Island, a small mound protruding above its surface. Samples dredged from the flank of the cone consist of hypersthene-angite andesite; samples from the mound consist of vitrophyric hypersthene-hornblende dacite. Arcuate fault planes enclose the caldera, but no fault scarps cross the floor, and there are no signs of any explosion craters.

INTRODUCTION

The first soundings of Crater Lake were made in 1886 by M. B. Kerr under the direction of Major C. E. Dutton (1889, p. 157). These soundings are reproduced on the U. S. Geological Survey topographic sheet of Crater Lake National Park (1:62,500 scale, edition of 1911 and successive reprints). Dutton noted two submerged, "abruptly rising prominences", one at a depth of about 450 feet and the other at a depth of 825 feet, but neither of these figures appears on Kerr's map. Subsequently, Diller (1902, p. 47) reported that the soundings, "together with information from Mr. W. G. Steel, who was present when the soundings were made", indicate two submerged cones, one of them close to the northern shore of the lake. According to this initial survey, the maximum depth of the lake was said to be 1996 feet.

The lake was sounded a second time during the summers of 1938, 1939, and 1940 by members of the National Park Service under the direction of John E. Doerr, Jr., then Park Naturalist. Their results were combined with the earlier ones to make the map reproduced by the present writer (1942, p. 109-111).

During July and August 1959, a third and much more exact series of measurements was made by the U. S. Coast and Geodetic Survey, using echosounding methods, with R. E. Williams as Chief of Party. Their detailed results have been simplified to make the contoured map shown as figure 1. During the summer of 1960, Ranger-Naturalist Carlton Nelson, guided by the new results, dredged samples from the flanks of two submerged cones, and these were kindly forwarded to me by the Park Superintendent, Otto M. Brown. Finally, I am indebted to Bennett Gale, Regional Chief of Interpretation, National Park Service, for securing consent to publish the following brief account.

NEW MAP OF THE CALDERA FLOOR

Perhaps the most striking feature revealed by the new map is the almost perfect cone near the northern margin of the caldera. This feature is here

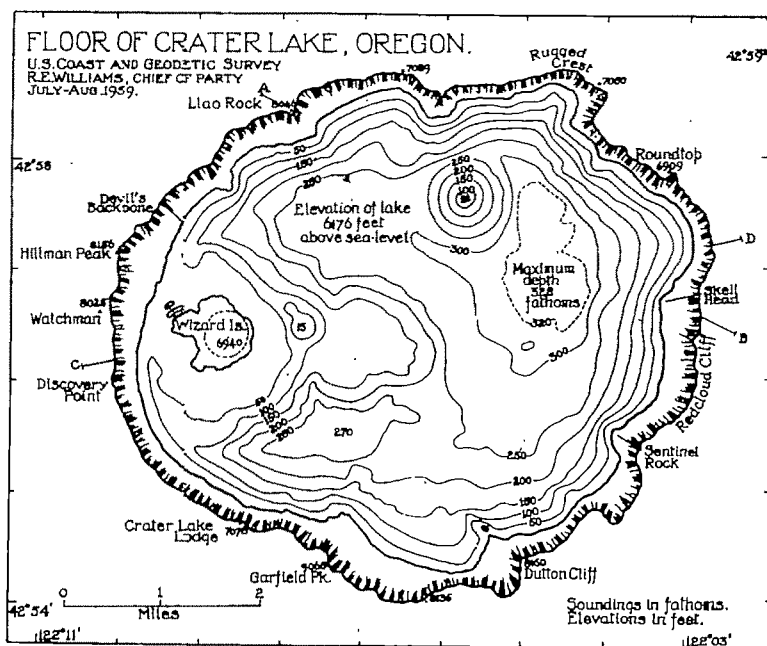


Fig. 1. Floor of Crater Lake.

named the Merriam Cone after J. C. Merriam, former President of the Carnegie Institution of Washington, in recognition of his leadership in promoting interpretation of the landscapes of the national parks, particularly of Crater Lake. The cone measures approximately one mile across the base and 1320 feet in height; in other words, it is almost precisely the same size as the new cone of Parícutín in Mexico. Moreover, the sides of the Merriam Cone slope at angles of 31° to 33° , as do those of Parícutín.

The absence of a crater at the top of the Merriam Cone suggests that toward the close of activity the explosions gradually diminished in intensity so that most of the final ejecta fell back into the vent; alternatively, the crater may have been filled by a mound of lava. At some stage during the growth of the cone, flows poured from fissures near the base, spreading southeastward over the floor of the caldera to form a lava plain more than a square mile in extent, with a maximum relief of no more than 12 feet. No doubt later falls of ash from the cone of Wizard Island have increased the smoothness of this lava surface, but the lack of pronounced ridges and depressions suggests that the flows were quite fluid and perhaps of pahoehoe type.

The angle of slope of the Merriam Cone denotes that the eruptions were subaerial; hence the cone must have started to grow shortly after the caldera was formed, approximately 7600 years ago, and before the level of the lake had risen very far. Samples obtained from the southeast flank of the cone by Carlton Nelson, using a drag-dredge, consist of dark, vesicular, porphyritic, and hyalopilitic hypersthene-augite andesite containing a few small olivines, and resembling closely some of the andesitic lavas of Wizard Island.

Kerr's original survey had already disclosed the presence of a submerged field of lava extending eastward from Wizard Island for about two miles. The recent survey indicates the limits of the field more accurately and shows a craterless, conical mound rising above the lava to a height of about 200 feet (figs. 1 and 2b). This mound may rest on the lava field; more likely it is only the topmost part of a much larger structure, most of which was buried by andesite flows from the cone of Wizard Island, just as the parasitic cone of Zapicho was buried by flows from the base of Parícutín. Surprisingly, samples dredged by Mr. Nelson from the flanks of the mound do not consist of andesitic cinders but of pale gray, vitrophyric hypersthene-hornblende dacite. This lava is much poorer in augite and richer in hornblende than is the adjacent dacite obsidian forming Liao Rock on the caldera wall, and resembles most closely the glassy dacites of Gleetwood Cove and Redcloud Cliff. The presump-

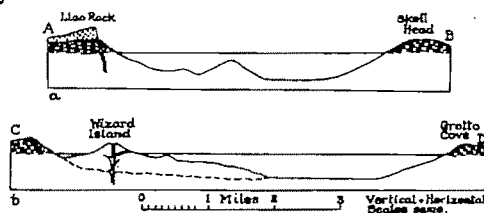


Fig. 2. Sections across Crater Lake. a. Section through the Merriam Cone and through the dacite obsidian flow and feeder of Liao Rock. b. Section through Wizard Island and the submerged flow to the east.

tion is, therefore, that the submerged mound east of Wizard Island marks the top of a Pelean dome; and perhaps the thick flow extending eastward from it was erupted at the same time and consists of similar dacite.

Cones and domes within calderas are often concentrated close to the walls, having been built over the marginal fractures, or they are disposed in lines parallel to structures in the subvolcanic basement, as seems to be the case, for example, in the Aso caldera of Kyusyu, Japan. But the line connecting Merriam Cone with the cone of Wizard Island and with the adjacent dome cuts at a high angle across the tectonic trends in the basement rocks, for these run approximately north-south, parallel to the length of the chain of High Cascade volcanoes.

Using isopach-maps of the ejecta around Parícutín as a guide (Segerstrom, 1950), it may be judged that the thickness of cinders laid down on the central part of the caldera floor by the eruptions of the Wizard Island and Merriam Cones nowhere exceeds 100 feet and is generally less than 50 feet. Much to be desired are drill holes and geophysical data to throw light on the configuration of the original caldera floor and on the attitudes of the fault planes that encompass the floor.

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WEATHERING AND SOIL FORMATION IN THE ARCTIC ENVIRONMENT*

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ABSTRACT. In order to depict the nature of the weathering processes operating in the arctic regions, four Arctic Brown soil profiles from northern Alaska were studied. Examination of the sand and clay fractions indicates that chemical weathering is in operation; its magnitude, however, is of a low order. Acid conditions in the surface facilitate the solution of carbonates, but their removal is incomplete as reprecipitation occurs within the profile. Because of increased concentration of iron-stained opaque minerals near the surface, oxidation of iron-bearing minerals was strongly indicated.

On very sandy quartzose profiles, iron, aluminum and manganese are partially mobilized and partially translocated, suggesting a weak podzolic process.

Clay-size minerals consist mainly of hydrous mica, kaolinite, chlorite, quartz, goethite, and feldspar. Hydrous mica, the most abundant clay mineral, was more hydrated at the surface and goethite was present only in the surface horizon. Alteration of feldspar into a claylike substance was noted, but well-crystallized feldspar persisted in the clay fraction.

A concentration of fines was present in the surface horizon of all Arctic Brown soil profiles. Whether this fine material forms *in situ* or is a result of aeolian deposition remains a moot question.

INTRODUCTION

Weathering of rocks and minerals, and the effect of rock composition on textural properties of the soil, have always held considerable interest for those engaged in arctic research. Until recent years most statements relating to weathering in cold environment were based largely upon field observations or limited laboratory data. Probably a factor inhibiting clarification of the problem was the complexity of arctic dynamics. Arctic areas tend to be mantled primarily with tundra or by shallow, rocky soils. Soils such as these are not particularly useful in studying pedologic processes because of high moisture content, shallow soil profiles, frost displacement, and related cryopedologic processes. If, however, studies are made on well-drained, mature soils, the effect of climate on the weathering processes can be properly appraised. This can be carried out in a manner similar to that used for Laterite, Podzol, Chernozem, and Desert soils. In the past few years, stable, well-drained soils which showed the full impact of the regional soil-forming factors were located (Dansereau, 1954; Drew and Tedrow, 1957; Karavaeva, 1958; Tedrow and Hill, 1955; Tedrow and others, 1958; Tedrow and Cantlon, 1958). These soils appeared to have morphology which depicts the regional zonal soil-forming processes.

Although the brown surface soils of the Arctic have been recognized, incidentally, for some time (Gorodkov, 1939; Grigorijev, 1930; Polyntseva and Ivanova, 1936; Sochava, 1933), it is only in recent years that a more complete

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Field studies were conducted by the authors under auspices of Boston University and were also aided by a contract between the O.N.R., Department of the Navy, and the Arctic Institute of North America. Reproduction in whole or in part permitted for any purpose of the United States Government.

picture was established. The genetic brown-colored soils have been designated by such names as Brown Tundra (Petrov, 1952), Arctic Brown soil (Tedrow and Hill, 1955), and Sod-Bare-Rock-Soil (Karavaeva, 1958). Drew and Tedrow (1957) presented analytical data on a single Arctic Brown soil profile showing the physical, chemical, and mineralogical nature of the soil, but it is unwise to extrapolate processes on a regional basis from a single site. Four additional Arctic Brown soils on widely different parent materials were, therefore, studied. An analysis of the data shows the nature of the pedologic processes operating in the well-drained sites of the arctic. In addition to the pedologic processes per se, the nature of the weathering processes in the arctic as a whole is evaluated.

WEATHERING AND PARTICLE SIZE

The precise nature of physical and chemical weathering in arctic regions has never been well established. The main consideration in this investigation, therefore, was to provide and interpret pedologic data and relate these data to weathering processes.

Glinka (1932) reported little apparent mechanical weathering of silts and sands in cold climates. Taber (1943) pointed out that, although mechanical disintegration is a primary factor in arctic weathering, it has been somewhat overemphasized. Gorodkov (1939) and Grigorijev (1930) shared the opinion that the weathering processes in the arctic regions are dominated by mechanical disintegration of the parent material, and that chemical processes are greatly subdued by the extremely low ground and air temperatures which inhibit both chemical and biological activity. More recently, Hopkins and Sigafos (1951) reported that particle size of the soil is largely controlled by the grain size of the rock. Blakemore and Swindale (1958) indicated that in the Antarctic soil-forming processes are barely discernible. Meinardus (1930), in his comparison of analyses of bedrock with the overlying shallow soils in Spitsbergen, clearly showed the weak podzolic character of the regional soil process. The work of Drew and Tedrow (1957) not only confirmed Meinardus' early work but also showed that there is a slight translocation of Fe, Al, and Mn in the profile together with the leaching of dolomite in the upper horizons. Tsyplenkin (1946) believed that chemical weathering involving carbonic acid, pH, acids excreted by roots, and products of hydrolysis is dominant. Meinardus (1930), in consideration of the weathering problem, found that the chemical processes involving oxidation of iron and solution of carbonates were quite prominent in some soils of the Spitsbergen tundra. Sochava (1933) reported that some soils of the Anabar River Basin tundras have calcareous C horizons, but no effervescing occurs in the upper horizons when treated with HCl. Polyntseva and Ivanova (1936) observed a slight movement of mobile iron in weakly podzolized soils of the Khibiny Massiv Tundras, forming a weakly developed illuvial horizon, which was enriched by secondary silicates and organic-alumina complexes.

Soil formation in the arctic regions is influenced by the presence of permafrost. Seasonal thaw approximates 18 inches or so over the vast areas of Arctic tundras but it may reach a maximum depth of about 40 or more inches

(Drew and others, 1958) in the well-drained sites. Because water movement in the active zone is restricted by the underlying permafrost, virtual saturation exists during the summer. The anaerobic conditions which result from water saturation show a predominance of the gley process. Mechanical mixing of organic and mineral portions of the soils acts over a very widespread area. In certain isolated locations representing a small areal extent, factors of relief and parent materials combine to permit a relatively deep thaw to occur. These areas occur most often on the crests of ridges, escarpment edges, river terrace edges, upper portions of stabilized sand dunes, and old beach ridges, where coarse sand and gravel predominate. Under these conditions, optimum drainage and aeration exist and there is maximum profile development.

Soils of the Alaskan arctic slope may be considered as a normal hydrologic series. The Arctic Brown soil is, in effect, the zonal soil of the area. In several very sandy places, however, incipient podzol development was observed. Under conditions of increasing wetness, tundra soil replaces the Arctic Brown soil. With increasing wetness of the site, hydromorphic soils such as Upland Tundra, Meadow Tundra, Half Bog, and Bog are present (Tedrow and others, 1958; Tedrow and Cantlon, 1958).

With increasing shallowness to bedrock and increasing coarseness of parent material, the Arctic Brown soils give way to Arctic Brown (Shallow Phase) soils and, finally, Lithosols and Regosols (Tedrow and Cantlon, 1958).

In order to determine the nature of chemical weathering processes operating in an arctic environment, it is necessary to examine those soils which exhibit the full impact of climatic forces. A study of several Arctic Brown and Arctic Brown (Shallow Phase) soils, which are quite stable, reveals the nature of the weathering.

The Arctic Brown soils form on a wide variety of parent materials, such as acid and calcareous sandstone, chert, gabbro, glacial till, loess, alluvium, and coastal plain sediments (Tedrow and Hill, 1955). Although the parent materials may be of diverse origin and composition, the acquired profile characteristics are similar.

One of the outstanding features of Arctic Brown soil is the color of the solum. It is quite distinctive and ranges from dark brown to dark reddish brown in the upper horizon to more yellow hues in the lower solum. The color change is usually gradual throughout the solum, but there is commonly a distinct color change marking the base of the solum. Mechanical analyses indicate that there is no translocation of clay within the profile, though a slight increase in clay content is usually noted at the surface. In many cases, this increase in clay content, together with a higher organic matter content, produces a fine crumb structure that grades into a single grain structure with depth. Most of the Arctic Brown soils that have developed on coarse sands and gravelly materials are devoid of compound structural characteristics.

DESCRIPTION OF SITES

Four Arctic Brown soils were collected in the Arctic Foothills for analysis.

A. Arctic Brown (Shallow Phase) on calcareous graywacke sandstone, near Umriat at 69°23'N, 152°10'W (table 1).

B. Arctic Brown (Shallow Phase) on gabbro on the east bank of the Nigu River at 68°30'N (table 2).

C. Arctic Brown on glacial till. About 5 miles east of the Nigu River at 68°29'N, 156°15'W (table 3).

D. Arctic Brown on a kame-terrace on the west side of the Kilik River at 68°30'N (table 4).

MATERIALS AND METHODS

Standard methods of sample collection and preparation were used (Kilmer and Alexander, 1949). The very fine sand (100-50 microns) fractions from all profiles were treated with bromoform (Sp.G. 2.85) to separate the heavy from light minerals. Slides for microscopic examination were prepared for the heavy and light minerals. Aroclor ($n = 1.66$) was used as an immersing medium for the heavy minerals and Canada balsam ($n = 1.54$) for the light minerals.

The heavy mineral identifications were accomplished with a petrographic microscope. Volume percentages of the recognized minerals were determined

TABLE 1
Morphology of an Arctic Brown (Shallow Phase) soil on calcareous graywacke sandstone—northern foothills section

Depth	Horizon	Morphology
2-0"	A ₀	Dark brown to black organic layer.
0-8"	A ₁	Dark gray-brown (10YR4/2) * very fine sandy loam, single grain to fine crumb structure. Some carbonate deposited on underside of rock fragments, pH 6.9
8-10"	A ₂	Gray-brown (10YR5/2) very fine sandy loam, loose single grain structure, weakly calcareous, pH 7.3
10-18"	C	Olive-gray (5Y5/2) very fine sandy loam, loose single grain structure. Many fractured bedrock fragments, moderately calcareous, pH 7.4
18" plus	D	Shattered bedrock, strongly calcareous.

* Munsell Notation, Munsell Color Company, Baltimore.

TABLE 2
Morphology of an Arctic Brown (Shallow Phase) soil on gabbro—southern foothills section

Depth	Horizon	Morphology
1/2-0"	A ₀	Dark brown to black organic matter.
0-4"	A ₁	Very dark brown (10YR2/2) sandy loam, loose single structure, pH 4.3
4-12"	A ₂ -C	Dark brown (10YR3/3) fine sandy loam, loose single grain structure. Numerous rock fragments. Transitional to C horizon, pH 5.0
12" plus	C	Dark brown shattered bedrock fragments of gabbro. Surfaces stained with rust-colored material.

TABLE 3

Morphology of an Arctic Brown soil on glacial till*—southern foothills section

Depth	Horizon	Morphology
1-0"	A ₀	Dark brown to black organic matter.
0-9"	A ₁	Dark brown to brown (10YR4/3) loam. Friable with crumb structure. Few till fragments, numerous roots. pH 3.5
9-14"	A ₂	Yellowish brown (10YR5/6) very fine sandy loam. Single grain to weak crumb structure. Few till fragments. pH 3.6
14" plus	C	Olive-brown (2.5Y4/4) loam. Compact, single grain structure. Many till fragments including quartzite, gabbro, sandstone, and siltstone. pH 4.7

* Anaktuvuk (?) Age (Detterman and others, 1958).

TABLE 4

Morphology of an Arctic Brown soil with minimal podzol development on kame-terrace*—southern foothills section

Depth	Horizon	Morphology
0-4"	A ₀	Very dark gray (10YR3/1) gravelly loam, loose single grain structure. Scant organic accumulation on surface. pH 5.7
4-24"	B	Dark yellowish brown (10YR4/4) gravelly very fine sandy loam, loose single grain structure. pH 4.7
24" plus	C	Brown (10YR5/3) gravelly loamy coarse sand, very loose single grain structure. Contains 66 percent gravel by weight. pH 5.0

* Ikkillik or Echooka (?) Age (Detterman and others, 1958).

by the field count method (Milner, 1952). The light mineral fraction was also examined. Staining methods for feldspar identification were employed with little success. An estimate of total feldspar content was made using only positive methods of identification such as refractive index, cleavage, and twinning features. Some feldspar undoubtedly escaped detection, but the primary interest lay in the detection of alteration products on the feldspar rather than the total content.

A thin section was made of a gabbro bedrock fragment found in association with the soil profile on the parent material. A modal analysis of its mineral content was determined using a petrographic microscope with a Hunt-Wentworth recording micrometer.

Portions of clay (<0.002 mm) were removed from all samples by decantation and treated with hydrogen peroxide to destroy organic matter. Coatings of iron and aluminum oxides were removed from the clay by Jeffries' method (Jeffries, 1947) prior to X-ray and differential thermal analysis. Clay identification by X-ray techniques was accomplished with a Norelco X-ray diffraction unit. Samples were packed in a thin-walled lithium glass capillary having an inside diameter of 0.2 mm. They were mounted in a Debye-

TABLE 5
Mechanical composition of Arctic Brown soils
(corrected to 100 percent)

Soil Profile	Parent Material	Horizon	Depth (inches)	Very Coarse Sand 2-1 mm	Coarse Sand 1-0.5 mm	Medium Sand 0.25-0.10 mm	Fine Sand 0.10-0.05 mm	Very Fine Sand 0.05-0.002 mm	Silt 0.002-0.001 mm	Clay <0.001 mm
Arctic Brown (shallow phase)	Calcareous graywacke sandstone	A ₁	0-8	6.4	7.5	8.7	19.1	22.3	27.8	8.2
		A ₂	8-10	5.3	7.0	9.4	21.9	24.0	23.4	9.0
		C	10-18	5.5	6.1	9.8	22.6	24.8	23.7	7.5
Arctic Brown (shallow phase)	Gabbro	A ₁	0-4	5.5	12.7	16.7	20.2	18.8	21.8	9.3
		A ₂ -C	4-12	4.8	8.2	10.7	17.5	12.7	36.2	9.9
Arctic Brown (normal phase)	Glacial till	A ₁	0-9	0.9	3.9	8.6	15.3	15.0	31.8	24.5
		A ₂	9-14	4.2	5.6	8.0	17.3	17.3	36.3	10.8
		C	14+	3.2	6.5	7.5	9.8	17.1	39.0	16.9
Arctic Brown (Minimal Podzol intergrade)	Kame-terrace	A ₂	0-4	1.3	1.6	3.8	14.1	26.8	40.5	11.9
		B	4-24	1.4	2.8	5.0	17.6	28.0	36.8	8.4
		C	24+	12.7	16.5	17.3	18.0	13.9	17.9	3.7

Scherrer powder camera (radius 57.3 mm) and rotated at one rpm for 6 hours in a primary X-ray beam using CuK ($\lambda = 1.54\text{\AA}$) radiation with a nickel filter at 35KV and 16 ma. Several samples were heated to specific temperatures in order to establish more positive identification of certain clay minerals.

Differential thermal reactions of clay samples were measured with thermocouples in an uncontrolled atmosphere heated from room temperature to 1020°C at a rate of 14°C per minute, using a Brown recorder.

pH values were estimated with a glass electrode-potentiometer system. Organic carbon was estimated by oxidation with chromic acid (Schollenberger, 1927). Cation-exchange capacities were determined by the methods of Peech and others (1947), and exchangeable sodium, potassium, and calcium were determined by the flame photometer method as outlined by Toth and Prince (1949). Exchangeable magnesium was determined gravimetrically by the $\text{Mg}_2\text{P}_2\text{O}_7$ method (Piper, 1947). The material removed from the clay was examined spectrochemically¹ for iron, aluminum, and manganese content.

RESULTS OF LABORATORY INVESTIGATIONS

Of the four profiles examined (table 5), three display an increase in the fine fractions (<50 microns) at the surface. This appears to be a common feature of the soils of well-drained environments (Drew and Tedrow, 1957; Tedrow and Hill, 1955). The reason for the increase in silt and clay at the surface of most profiles is not known. Wind action alone cannot be given as a sole explanation of the origin of the increased quantity of fines at the surface because there is a marked uniformity of the heavy mineral suites among the various horizons of the individual profiles. On the other hand, increase in fines at the surface cannot be ascribed entirely to weathering.

The gabbro profile showed an increase in silt content with depth, but the clay was constant. The light mineral fractions consisted of quartz, feldspar, chert, and others (fig. 1).

The mineral components of the Arctic Brown (Shallow Phase) soil on sandstone (fig. 1) indicate that the heavy mineral content was relatively constant throughout the profile at 1.5 percent. Biotite, high in iron, was a prominent heavy mineral and increased from 6 percent in the A_1 horizon to 21 in the C. Many of the opaque heavy mineral grains had a micaceous habit. Biotite did not actually diminish at the surface, but many grains were masked with iron and organic coatings rendering them opaque. Apatite had its greatest concentration in the A_2 horizon and decreased slightly in both A_1 and C horizons. The apatite grains were strikingly euhedral in shape with crystal habit consisting of prismatic shapes and hexagonal basal plates. Interfacial edges were very sharp and showed no evidence of solution.

Dolomite fragments were virtually restricted to less than 100 microns in size. They were irregular in shape and probably represented fragments of cementing material of the sandstone. The most significant feature was that dolomite fragments were totally absent in the A_1 horizon. There was about 4 percent in the A_2 horizon and an increase to 6 percent in the C horizon. Car-

¹ Spectrochemical analysis by N. F. Shimp.

bonate material has been leached from the surface horizon. Other heavy minerals identified in minor quantities were muscovite, tourmaline, zircon, chlorite, sphene, diopside-augite, garnet, and rutile.

The opaque, heavy mineral grains, many of which displayed a micaceous habit, were predominantly yellowish or reddish brown in color. Their percentage increased toward the surface, possibly indicating that a greater oxidation of iron had taken place in the upper horizons.

The light fractions of the sandstone profile showed that the identifiable feldspar content approximated 10 to 13 percent throughout the profile. For the most part, the feldspar was relatively fresh in appearance, although some grains had a claylike substance concentrated on the surface or along cleavage cracks. Orthoclase and plagioclase feldspars were present in about equal amounts throughout the profile. The majority of light mineral opaques appeared to be shale fragments and clay aggregates. The heavy mineral fraction

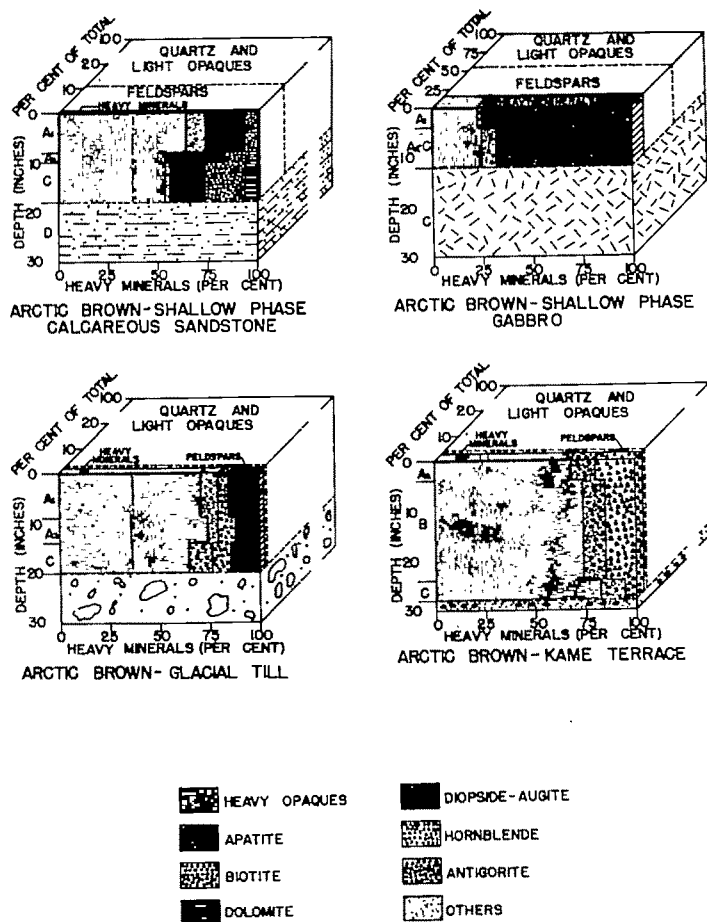


Fig. 1. Mineral composition of the very fine sand fractions of four Arctic Brown soils.

on the Arctic Brown (Shallow Phase) soil on gabbro (fig. 1) was extremely large in comparison to the other profiles examined, but this was not too surprising as the parent material was dominated by the ferro-magnesian mineral augite. The heavy mineral content ranged from 15 percent at the surface to 13 in the A_2 horizon. Of the heavy minerals, augite contributed by far the greatest quantity, ranging from 75 percent at the surface to 68 percent in the A_2 horizon. Examination of the gabbro thin section revealed that antigorite was present, but it appeared to be a hydrothermal alteration product of the augite and not the result of normal weathering processes. Its presence was due merely to mechanical disintegration of the bedrock.

Other heavy minerals present in minor quantities were chlorite, hornblende, zircon, garnet, muscovite, rutile, and tourmaline. Magnetite was also present in the heavy mineral fraction.

The opaque heavy minerals included many reddish and yellowish brown particles which were probably augite grains stained by iron-organic complexes. The content of opaque heavy minerals was higher in the A_2 horizon than in the surface A_1 horizon.

The light mineral fraction contained about 50 percent feldspar, and, from the X-ray analysis, the feldspar appeared to approximate the composition of oligoclase. An appreciable quantity of quartz was present in the profile and was thought to have been deposited by aeolian activity. Quartz was not a component of the underlying bedrock.

The mineral components of the Arctic Brown soil on glacial till given in figure 1 shows that heavy mineral fraction approximated 2 percent of the very fine sands with a slight increase occurring with depth. Diopside-augite represented the major portions of the identified heavy mineral fraction, approximating 12 to 15 percent. In addition, 5 to 8 percent hornblende was also present in the very fine sand fractions. Other heavy minerals present in minor quantities are epidote, tourmaline, chlorite, sillimanite, rutile, biotite, kyanite, apatite, sphene, hypersthene, actinolite, muscovite, and dolomite. There was little variation in the profile with respect to the assemblage of heavy minerals.

The opaque minerals comprised a large portion of the heavy mineral fraction. Their distribution increased from 71 percent in the A_1 horizon to 74 percent in the A_2 and decreased to 64 percent in the C. Many of these opaque grains had moderate magnetic properties and were undoubtedly magnetite and partially altered ilmenite. A great many of the opaques were heavily stained.

The feldspar content of the light fraction approximated one percent. Most feldspar was relatively fresh, with some alteration along cleavage cracks. Quartz and chert comprised the major portion of the light minerals.

The mineral components of the Arctic Brown soil on the kame-terrace is shown in figure 1. The heavy mineral content ranges from 2.5 percent in the A_2 and B horizons to about 1.5 percent in the C horizon. The major portion of nonopaques is antigorite. This mineral decreases from 20 percent in the A_2 horizon to 6 percent in the C horizon. Chlorite, also present in smaller quantities, has the same distribution pattern. Other heavy minerals present in minor quantity are diopside-augite, zircon, muscovite, biotite, garnet, hornblende, rutile, tourmaline, chloritoid, apatite, and actinolite.

In the fine sand heavy mineral suite, opaques were dominant; increasing with depth from 68 percent in the A₂ to 82 in the C horizon. Most grains ranged in color from yellowish brown to reddish brown to dark brown. Many grains were probably altered ilmenite and heavily stained nonopaques.

The feldspar content was very low, approximating one percent, and was relatively free from alteration products on the surface or in cleavage cracks.

CLAY MINERALOGY

X-ray diffraction patterns of the soil clays indicated that hydrous mica, kaolinite, and quartz were present in all profiles (table 6). Feldspar was present in the Arctic Brown (Shallow Phase) soil on calcareous graywacke sandstone and gabbro. Chlorite was present in the profile on the kame-terrace.

TABLE 6

Clay and clay-size minerals present in Arctic Brown profiles

Arctic Brown (Shallow Phase) on Calcareous Sandstone			
	A ₁	A ₂	C
Hydrous Mica*	++	++	++
Kaolinite	+	+	+
Feldspar	+	+	+
Quartz	+	+	+
Goethite	+	-	-
Arctic Brown (Shallow Phase) on Gabbro			
Clay-Size Minerals	A ₁	A ₂ -C	
Hydrous Mica	++	++	
Kaolinite	+	+	
Feldspar	+	+	
Quartz	+	+	
Goethite	+	-	
Arctic Brown on Glacial Till			
Clay-Size Minerals	A ₁	A ₂	C
Hydrous Mica	++	++	++
Kaolinite	+	+	+
Quartz	+	+	+
Goethite	+	-	-
Arctic Brown on Kame-Terrace			
Clay-Size Minerals	A ₂	B	C
Hydrous Mica	++	++	++
Chlorite	+	+	+
Kaolinite	+	+	+
Quartz	+	+	+

* A₂ as defined by Brindley, G. W., *The X-ray Identification and Crystal Structures of Clay Minerals*: Mineralogical Society, British Museum, London, 1951, p. 55.

profile only. Goethite was present in all profiles except the one on the kame-terrace. It is significant to note that this mineral was found only in the surface horizon. All clay-size minerals are thought to be primarily allocthenic, with the exceptions of goethite and the "claylike" substances associated with the feldspars. Goethite was probably the result of oxidation of iron-bearing minerals in situ. Hydrated mica was the dominant clay mineral in the profiles examined. Its broad halo at 10Å indicated its hydrated nature. Upon heating clay samples to 700°C, water was removed and the halo disappeared, resulting in a sharp line at 10Å. The other clay-size minerals were probably present in minor amounts.

Differential thermal curves of soil clays in the four profiles are used to

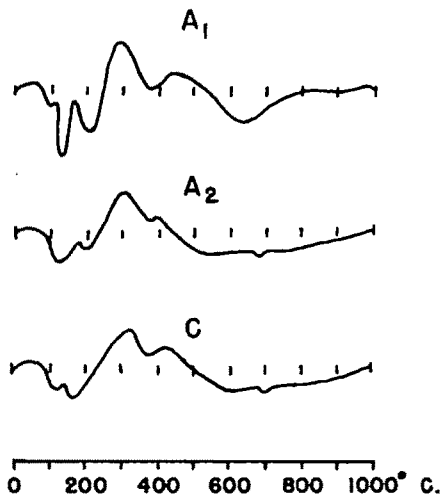


Fig. 2. Differential Thermal Analysis -
Calcareous Sandstone Profile

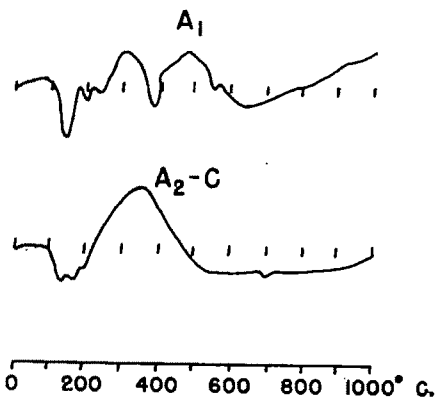


Fig. 3. Differential Thermal Analysis -
Gabbro Profile

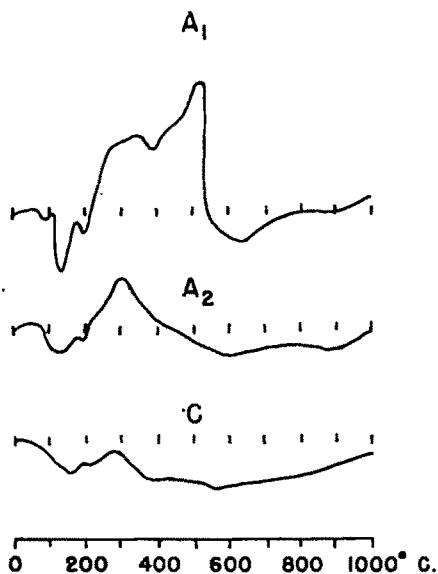


Fig. 4. Differential Thermal Analysis -
Glacial Till Profile

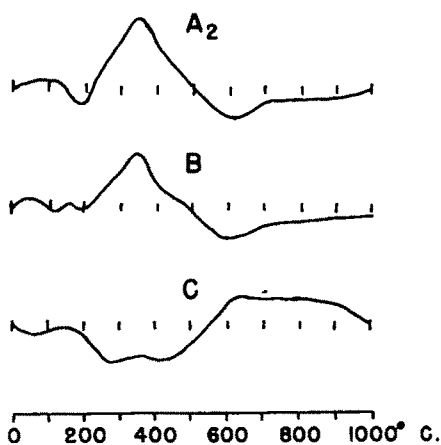


Fig. 5. Differential Thermal Analysis -
Kame Terrace Profile

supplement clay mineral identification and are given in figures 2 through 5. Figure 2 shows that in the Arctic Brown (Shallow Phase) soil profile on calcareous graywacke sandstone there are three distinct endothermic reactions at low temperatures which represent the loss of absorbed and interlayer water from the clays. The water loss at 90°C may have been the water absorbed by the residual organic substances present; that which was lost at about 125°C represented the loss of absorbed water on the clay particle itself, whereas that

lost at 200°C represented water removed from the interlayer positions. The intensity of the dehydration curve seemed to indicate a higher degree of hydration in the surface horizon. Only two endothermic peaks were noted in the A₂ and C horizons, and they are not sharp. The exothermic reaction, whose peak ranges from 290°C at the surface to 310°C in the C horizon, was attributed to the presence of organic matter. The endothermic reaction, occurring at about 370°C to 380°C, was attributed to the presence of goethite.

The endothermic reaction in the A₁ horizon at about 630°C and the exothermic reaction at about 900°C were attributed to kaolinite. These peaks, poorly developed, indicated poor crystallinity or small quantities of kaolinite. No distinct thermal reactions were noted in the A₂ and C horizons above 500°C.

Differential thermal curves of the Arctic Brown (Shallow Phase) soil on gabbro are given in figure 3. A triple dehydration curve was present in both samples, although it occurred over a wider temperature range than the previous profile. The peaks were more distinct in the A₁ horizon than in the A₂-C horizon. The strong exothermic reaction due to the presence of organic substances occurs in both the A₁ and A₂-C horizons but was markedly interrupted in the A₁ horizon by a strong endothermic reaction at 380°C. This was attributed to the presence of goethite.

Figure 4 shows the differential thermal curves of soil clays from the Arctic Brown soil on glacial till. Dehydration occurred up to 200°C and is more pronounced in the A₁ horizon than in the A₂ or C horizons. The exothermic reaction, due to the presence of organic residues, was pronounced in the A₁ horizon and decreased in intensity with depth. An endothermic reaction at 375°C occurred only in the A₁ horizon and is thought due to goethite. An endothermic peak occurred at 630°C in the A₁ horizon, and at 570°C in both the A₂ and C horizons, but they were too ill defined for speculation as to contributing agents.

The results of differential thermal analyses on soil clay from the Arctic Brown soil profile on the kame-terrace, presented in figure 5, indicate that the low temperature endothermic reactions due to the dehydration of the clays were quite small. The X-ray diffraction patterns also showed this low degree of hydration since the usual diffuse halo at 10Å was absent. A sharp, well-defined line was present instead. No other significant thermal reactions were noted in this profile except the prominent exothermal reaction accompanying the oxidation of organic matter in both A₂ and B horizons.

SOIL CHEMISTRY

The Arctic Brown soil profile on the kame-terrace had a thin but distinct bleicherde, indicating a trend toward podzolization. In order to aid in establishing the podzolic character of this soil, partial chemical analyses were made. Table 7 shows that the cation exchange capacity is high in the A₂ horizon and decreases with depth. Differences within the profile appear to follow the organic matter content closely, a condition that might be expected due to the paucity of clay. The exchangeable Ca, Mg, Na, and K were also determined. Calcium and magnesium contributed the greatest amounts of exchangeable

TABLE 7

Chemical data from Arctic Brown profile on kame-terrace showing evidence of minimal podzol development

Horizon	O.M. Content (Cx1.72)	C.E.C./ 100 gms. soil me.	Exchangeable Cations				Base Saturation %	pH	Material Removed From Clay-Jeffries Method		
			me. per 100 gms. soil						Fe ₂ O ₃ %	Al ₂ O ₃ %	Mn ppm.
			Ca	Mg	Na	K					
A ₂	15.9	26.6	12.30	5.68	Tr.	0.47	69.4	5.7	4.23	1.10	224
B	4.3	10.2	2.42	1.34	Tr.	0.33	40.1	4.7	17.85	3.55	686
C	2.5	7.4	2.88	0.98	0.02	0.21	55.3	5.0	13.76	3.40	1430

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Chemical data from Arctic Brown profile on kame-terrace showing evidence of minimal podzol development

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			Ca	Mg	Na	K			Fe ₂ O ₃ %	Al ₂ O ₃ %	Mn ppm.
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B	4.3	10.2	2.42	1.34	Tr.	0.33	40.1	4.7	17.85	3.55	686
C	2.5	7.4	2.88	0.98	0.02	0.21	55.3	5.0	13.76	3.40	1430

bases throughout the profile. It was also noted that the pH of this horizon was lower in comparison with that of the A_2 and C horizons. Some bases in the A_2 horizon might have been liberated from the organic matter by leaching with ammonium acetate, thus masking the true base-exchange status of this horizon.

Clay coatings removed by the Jeffries' method were analyzed spectrochemically for iron, aluminum, and manganese. The iron and aluminum complexes on the clay surfaces were low in the surface A_2 horizon. An increase of iron and aluminum coatings in the B horizon was observed, whereas only a slight decrease occurred in the C horizon. Manganese increased quite markedly with depth.

DISCUSSION

Chemical weathering in arctic regions is best typified in the deep, stable, mature soils, because thaw occurs earlier on these sites (Drew and others, 1958) and soil temperatures and attendant biological activity are higher than on the adjacent poorly drained areas. Although there is positive evidence of chemical weathering processes in operation in these well-drained areas, it must be pointed out that because of low temperatures the processes operate at a slow rate.

The podzolic process is in operation in the Arctic Brown and related soils but usually can be detected only by laboratory analyses. Of the four soils studied, the Arctic Brown soil on the kame-terrace material showed the most advanced stage of podzolization. The profile displayed a thin bleached A_2 horizon characteristic of minimal Podzol soils. Soils of this nature are rarely found on the Arctic Slope and are thought to develop only under special conditions: coarse-textured, highly quartzose, acid parent materials.

Chemical activity may be embodied in several processes. Solution is evi-



Fig. 6. Precipitation of carbonates on the underside of sandstone. Rock sample taken from the A_1 horizon of Arctic Brown soil. Reprecipitation of white carbonate crusts or brown-to-black organic stained carbonate crusts may occur in the upper 40 inches of the profile.

dent in the Arctic Brown (Shallow Phase) soil on calcareous graywacke sandstone. Carbonates present in the parent material have been leached from the surface horizons. The removal of carbonates is not, however, complete as reprecipitation commonly occurs. Evidence of this may be seen in figure 6, where the carbonates are shown precipitated on the underside of a calcareous graywacke sandstone fragment that was found near the surface adjacent to the profile.

Oxidation is also prominent in the soils of the well-drained environment. This is evident from the strong brown colors in the upper soil horizons. A large number of reddish brown and yellowish brown opaque minerals in both the heavy and light mineral fractions were present. Oxidation of iron in magnetite and ilmenite is prevalent and is also noted in such iron-bearing non-opaques as augite and biotite. In the Arctic Brown soils with thicker horizons, percentages of opaques increased with depth or were best expressed in the B horizon. This may be due, in part, to the downward movement and reprecipitation of soluble iron and organic complexes masking many of the nonopaque grains. Effects of oxidation may also be seen in figure 7 as a weathered rind occurring on a piece of graywacke sandstone. The weathered rind is rusty brown in color; the middle portion is the normal gray color. Although the weathering is not intense, it represents the partial oxidation of iron-bearing minerals in the rock.

X-ray and differential thermal analyses of soil clays show that hydration is quite active in the well-drained sites and appears to be intensified somewhat at the surface. From differential thermal analyses endothermic reactions at low temperatures were more pronounced in surface clays, whereas at lower depths they were less intense and poorly defined.

Iron oxides are also in a more hydrated state at the surface. It was noted that the endothermic reaction occurring between 380°C and 400°C, attributed to goethite, was usually present only at the surface or was more intense at the surface than in lower horizons.

Hydrolysis, associated with clay mineral formation in the soil, appears to be poorly expressed under the arctic environment. X-ray diffraction patterns of soil clays reveal that clay types are rather consistent throughout the profile. The only clay minerals that may be forming in situ by hydrolysis are those associated with the feldspars and possibly some of the iron-bearing minerals. The quantity present is small and appears to be confined primarily to mineral surfaces and cleavage cracks. The mere fact that feldspar is present in the clay fraction supports the theory that the hydrolytic process is not strongly developed. In temperate climates feldspar is seldom present in the clay fraction of materials of comparable age. Most of the clay present in the profiles is thought to be of allogenic origin.

The predominance of silty textured soils in the arctic has led many investigators to believe that mechanical disintegration is the main force responsible for the occurrence of this predominating texture. Mechanical disintegration of parent materials, whether it occurs during transportation or in situ, is active not only in the arctic regions but in the temperate regions as well. The primary mechanisms of mechanical disintegration are frost-riving and differential ex-



Fig. 7. Weathering rind of a sandstone fragment. The weathered rind is rusty brown while the central core is gray-colored.

pansion of mineral components, due to temperature fluctuations. Forces resulting from freezing and thawing and consequent expansion and contraction cause gross disintegration of parent materials. It is suggested that these forces would be more active in temperate zones where diurnal temperature fluctuations are greater. The arctic environment, although characterized by extreme seasonal temperature variations, does not have wide diurnal fluctuations, which might tend to minimize the effect of repeated expansion and contraction of the mineral constituents of the parent material (Conover, 1953).

Mechanical disintegration does, however, play an important role in the formation of the predominantly fine textures of arctic soils. In glacially transported materials, gross disintegration occurs during periods of active transportation. The grinding effect of materials incorporated in ice is well known. To a lesser extent further mechanical disintegration may occur if glacial deposits are reworked by fluvial action.

The magnitude of mechanical disintegration in situ largely depends upon the nature of the parent material. The rocks which predominate in the Arctic Slope of Alaska consist of poorly consolidated porous sandstones and shales.

DISCUSSION

ACCRETION-GLEY AND THE GUMBOTIL DILEMMA

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The paper being discussed (Frye, Shaffer, Willman, and Ekblaw, 1960) should be read carefully by all Pleistocene geologists and by soil scientists working in continentally glaciated areas, for it has to do with facts, principles, and terms that are of much use in working out the glacial and interglacial history of the Pleistocene.

Gumbotil as defined (Kay, 1916a, 1916b; Kay and Pearce, 1920) is well known to Pleistocene geologists. The identification and interpretation of gumbotil in Iowa have helped materially in differentiating the Nebraskan, Kansan, Illinoian, and Wisconsin drift sheets and in establishing the current Pleistocene classification in glaciated North America. More than 150 exposures of gumbotil have been observed in Iowa (Kay and Apfel, 1929; Kay and Graham, 1943), and more than 40 sections showing relations of gumbotil to underlying till have been measured and described in detail. Samples from 11 members of these sections have been subjected to laboratory analysis. The authenticity of none of these occurrences is questioned in the paper under discussion. To be sure, most of these particular exposures are now covered. This is inherent in glacial and interglacial materials. However, new exposures that show the same essential characters appear temporarily from time to time.

Definitive characters of gumbotil are given below. Gumbotil is (1) compact clay, sticky when wet, and hard when dry; (2) completely leached; (3) contains little or no easily weatherable material except near the base; (4) breaks up when wet into small, starchy, polyhedral pellets with shiny sides, the "soil structure" of modern soil science (Soil Survey Manual, 1951, p. 225-230); (5) is massive not stratified; (6) seldom exceeds 15 feet in thickness; (7) contains pebbles of rocks and minerals that are difficultly weatherable, such as quartz, chert, and quartzite similar to pebbles in underlying till, and these pebbles become gradually larger and more numerous from top to bottom; (8) nowhere lies directly on fresh till but grades downward through oxidized and leached and oxidized and unleached to unoxidized and unleached till; (9) contains "ghost" pebbles, cobbles, and boulders of crystalline erratics, especially in its lower part; (10) except where uncovered by erosion is overlain by unweathered or only slightly weathered till or loess. Of these characters number (8) is particularly important. Taken together they constitute a specific definition that includes all gumbotils and excludes all nongumbotils. The term "gumbotil" by definition is applicable only in areas that have been glaciated, and exclusively to glacial geology.

These facts led Kay and his associates to the conclusion that gumbotil resulted from long-continued weathering of till following deposition by an ice sheet before being covered by material deposited from a much younger ice sheet. Is this "dogma" (Frye and others, 1960, p. 185) or an approved method of scientific investigation?

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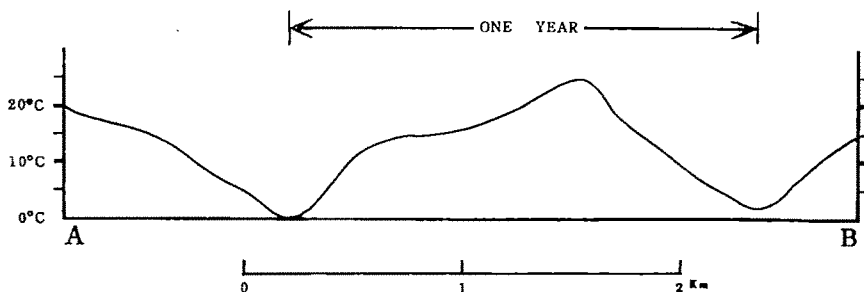


Fig. 5. Variation of "original" temperature in section A-B in figure 4 (ordinate: temperature of water on entry underground).

flows farther. (2) The clay bed known at station 2 does not extend as far up-stream as station 1 (fig. 2). Therefore, ground water in this area is believed not to be confined.

The fact that the measured velocities decrease downstream may be due to the decrease of hydraulic gradient and/or to the increased thickness of the aquifer.

Some practical remarks on the method are the following: (1) The amount of dissolved nitrogen can vary for biochemical reasons in a field where ammonium or nitrate ions are found in appreciable quantities. Thus nitrogen would not be appropriate as a tracer in such a field. (2) Successive measurement is favorable in a field where suitable wells are rare, but cannot be applied if it takes more than one year for water to move from one test well to another. Simultaneous measurement has the advantage that the velocity can be determined in a short period of time, but it cannot be applied to a field having only a few wells. In any case, it is necessary to select test wells that belong to the same aquifer. (3) The application of this method is restricted to fields where water is supplied from a limited source and the direction of ground water current is known. In the case where several water masses contribute to the aquifer at different points, it will be difficult to use this method. On the other hand, if the contaminating water mass is relatively small, simultaneous measurement may detect it, for such a contamination should be indicated by distortion of the contour lines of dissolved argon. (4) From a geochemical point of view, it would be interesting to compare this method with the natural tritium method, because both are suitable for ground water moving through large areas with seepage times measured in years.

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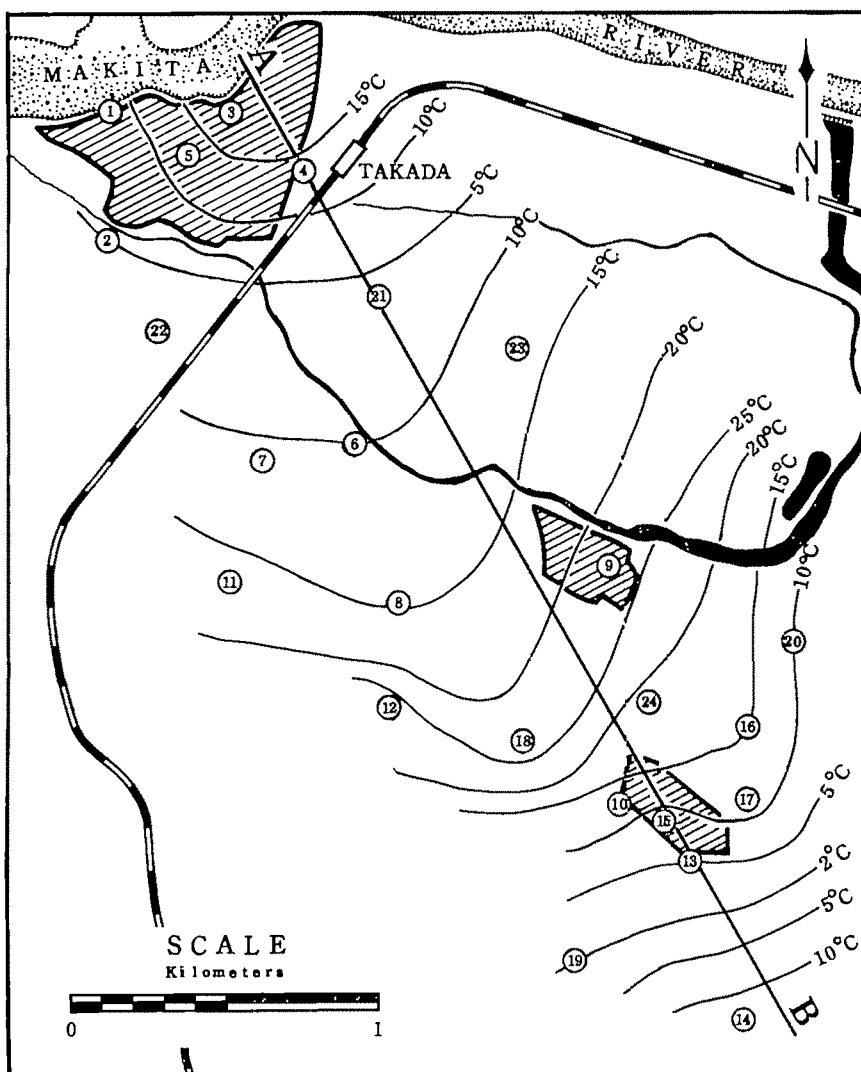


Fig. 4. Contour lines of "original" temperature of ground water; circled numbers are numbers of stations in table 2.

The results from the two methods of observation, successive and simultaneous, are self-consistent, indicating that the methods are reliable.

In table 1, the velocity from station 1 (river) to station 2 (test well 1) is very large. This large value is mainly caused by inexactness in estimating the distance between stations: (1) Water taken at station 1 is surface water, and uncertainty is inevitable about the starting point of seepage; that is, river water is always observed at station 1, even in the dry season, and it disappears from the river bed just beyond this station, but in the rainy season it

culated from the argon content observed. Temperatures calculated in this way are shown in table 2.

The contour lines (isopleths) in figure 4 show the distribution of the temperature values so calculated. Figure 5 shows the relationship between the "original" water temperature and ground water movement along section A-B. The distance interval from one minimum temperature to the next minimum in this curve corresponds to a time period of one year. The effective velocity of ground water between the test wells used for the successive measurement is recalculated on the basis of the simultaneous measurements, and the results are given in table 3.

TABLE 3
Effective velocity by simultaneous measurement

Station*	Distance in meters	Time Interval in months	Effective Velocity in meters/day
2-3	1500	6	8.4
3-4	1100	7	5.8

* Stations have the same number as in table 1.

TABLE 4
Converted velocity (by Darcy's formula*) for a one percent hydraulic gradient

Station†	Hydraulic Gradient** (percent)	Converted Velocity (meters/day) Successive Measurement	Simultaneous Measurement
2-3	0.2	51	42
3-4	0.1	36	58

* Darcy's formula is $V = k \cdot h/l$, where V is effective velocity of ground water, h/l is hydraulic gradient, and k is constant.

** Value published by Murashita and others (1954).

† Stations have the same number as in tables 1 and 3.

DISCUSSION AND CONCLUSIONS

It may not be fair to use Darcy's law to compare the present result with data published by other investigators, because the test aquifer contains very coarse gravels (1 cm to 50 cm in diameter) with small amounts of pebbles and sand, whereas Darcy's law is usually applicable to fine-grained sand beds. However, if we assume that Darcy's law can be applied to such an aquifer, and use the hydraulic gradient published by Murashita and others (1954), the present result can be converted into the velocity for a one percent hydraulic gradient (table 4). Tolman (1937, p. 219) published the value of 33 meters per day as the average velocity in coarse gravel for one percent hydraulic gradient. Usually the average velocity is a little lower than the effective velocity. Therefore, the effective velocities observed (36 to 58 meters per day) seem to be reasonable.

the time-displacement of the maximum value of dissolved nitrogen and argon between one station and the rest, the velocity of ground water flow is calculated. It takes two months for ground water to reach test well 1 after sinking underground; five months to move from test well 1 to test well 2; ten months from test well 2 to test well 3. The effective velocities are calculated from these time intervals and the distances between the stations as shown in table 1.

Simultaneous measurement of dissolved argon.—On the basis of the principle mentioned above, 24 wells were selected in this field, and dissolved argon was measured during a short period between May 28 and June 12, 1958. The result is shown in table 2. Argon is perfectly inert, so we can trace its behavior without any interference from chemical reactions. Oana (1957) determined the content of dissolved argon in water which is in gas exchange equilibrium with air under 1 atmosphere pressure. His results suggest that the temperature of water at the time when it soaked into the ground may be cal-

TABLE 2
Dissolved argon content and estimated "original" temperature of water
by simultaneous measurement

Station number	Dissolved argon content ml/L	"Original" temperature of water** °C
1	0.38	9
2	0.42	5
3	0.32	17
4*	0.34	14
5	0.34	14
6	0.37	10
7	0.36	11
8	0.33	15
9	0.28	23
10	0.35	13
11	0.30	17
12	0.26	27
13	0.42	5
14	0.35	13
15	0.41	7
16	0.33	15
17	0.36	11
18	0.28	22
19	0.46	2
20	0.37	10
21	0.43	4
22	0.47	0
23	0.34	14
24	0.31	17

* Station 4 is test well 1 in table 1.

** Temperature of water on entry underground is calculated from Oana's measurements (1957) of solubility.

Three test wells were chosen; they are located along the supposed direction of flow and belong to the same aquifer (fig. 2). Nitrogen and argon were determined in each well water once a month during the period between February 1955 and March 1956.

TABLE 1
Effective velocity by successive measurement

Station*	Distance in meters	Time Interval in months	Effective Velocity in meters/day
1-2	5000	2	84
2-3	1500	5	10
3-4	1100	10	3.6

* Station 1, Makita River; station 2, test well 1; station 3, test well 2; station 4, test well 3.

Figure 3 shows that test well 1 (station 2) has a maximum value in April and a minimum in October; test well 2 (station 3) has a maximum in September; test well 3 (station 4) has a maximum in July and a minimum in

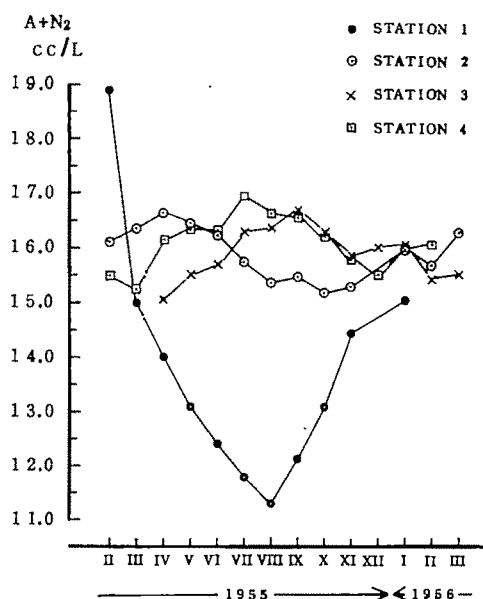


Fig. 3. Successive variation of dissolved nitrogen and argon in river water (station 1) and test well water.

December. Also shown in this figure (station 1) is the variation of nitrogen and argon in river water at the spot where Makita River water disappears from the bed. The maximum is in January when the water temperature is 4.7°C and the minimum in August when the water temperature is 25°C. From

character of the ground water changes in that direction; that is, its content of sodium, potassium, total cations and bicarbonate increases in that direction, while calcium and magnesium decrease.¹

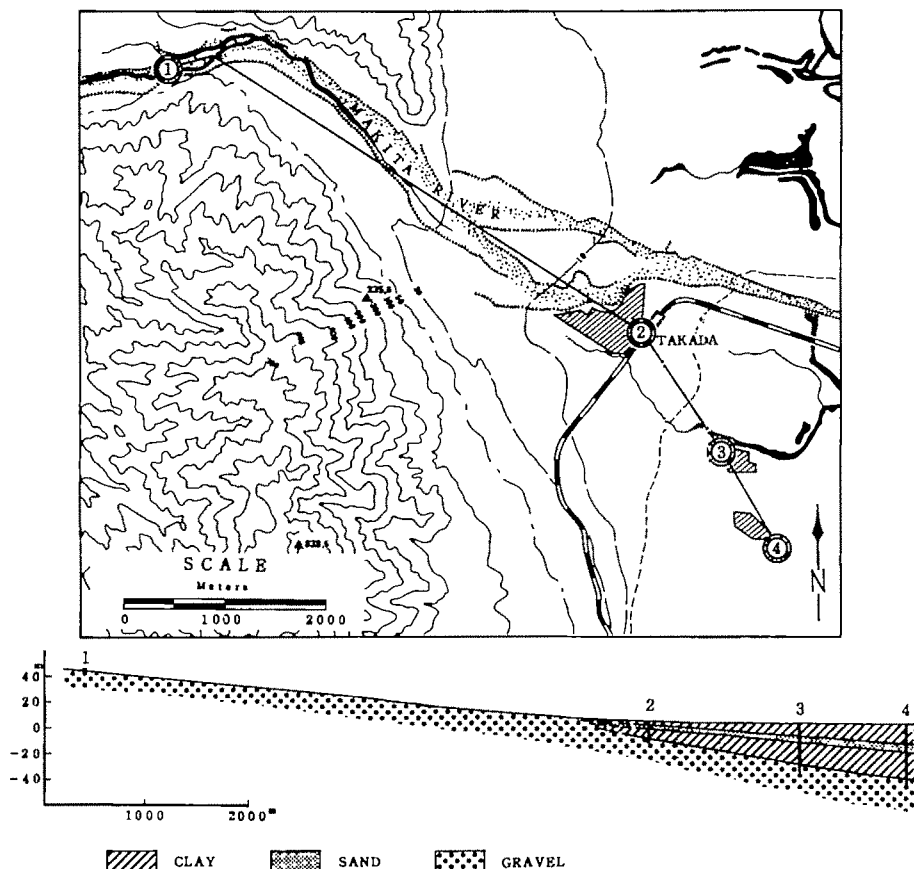


Fig. 2. (Above) topographic map showing locations of samples for successive measurement; (below) geologic section showing well depth.

RESULTS

Successive measurement of dissolved gases.—The mass-spectrometric determination shows that the content of dissolved methane is very low in this field; its maximum value is only 0.05 ml/L. No higher hydrocarbons were detected. Therefore the dissolved gases, after oxygen is subtracted, consist of nitrogen and argon. The amount of dissolved nitrogen may change due to denitrification of nitrogen-containing compounds and to the fixation of nitrogen. In this area, however, where the production of methane is very weak, we can expect no appreciable change of dissolved nitrogen. Nitrogen and argon can therefore be used as tracers.

¹ This may be due in part to base exchange. However, the increase of sodium and potassium exceeds the equivalent amount expected after base exchange. The excess may be derived from specific dissolution of sediment.

temperature. The content of dissolved gases as observed in the ground water is more or less smoothed, probably because of gas diffusion and mixing of water. However, where the difference in water temperature between winter and summer is considerable, the variation of dissolved-gas content can be detected in ground water. When the content of dissolved gases in water taken from the same well is successively measured, revealing its maximum and minimum in a year, we can deduce the time of year during which each sample entered the ground. Oana pointed to the usefulness of argon as a tracer for this purpose; argon is inert and never undergoes any chemical reaction in the ground. Oana (1954, 1957) measured successive variation of dissolved argon in water from some confined wells in Nagoya and Matsumoto.

METHODS

Principle of the present method.—Even if a maximum of gas content appears in water, we cannot always tell the year of its initial permeation. If more than one year has elapsed since the water soaked into the ground, we cannot decide whether a maximum of dissolved gases means the preceding winter. The method must therefore be applied in a field where the source of ground water is well known and where the direction of water movement is easily estimated. Further development of Oana's method was tried by the following two ways, which were then compared: (1) The test wells chosen were situated along the direction of ground water flow, and the amount of dissolved gas was measured in each well every month; the effective velocity of ground water was estimated from the lapse of time for attainment of maximum dissolved-gas content. (2) The amount of dissolved gases was measured in many wells at about the same time, and isopleths were drawn. From the locations of maximum and minimum values of dissolved gases the effective velocity of the ground water movement was estimated.

Sampling and experimental methods.—Water samples were taken from artesian wells by inserting the tip of a siphon about two meters below the casing head in order to avoid contact with air. Dissolved gases are driven out of the water sample by means of Winkler's carbon dioxide method as modified by Sugawara (1939). The total volume of dissolved gases minus carbon dioxide is measured manometrically. Oxygen is determined next by difference after absorption by an alkaline pyrogallol solution. The remaining gases are determined mass-spectrometrically.

Description of the field.—The foregoing methods were applied to the field around the town of Takada, in the prefecture of Gifu. In this region the Makita River runs into an alluvial plain from a mountainous hinterland composed of Permo-Carboniferous rocks (fig. 1). Except during the rainy season, the river ceases to flow on the surface at or below its point of entrance onto the plain. Water that disappears from the river bed is supposed to become confined water beneath the alluvial plain. This ground water should flow southeastward in the direction of the surface slope, for the following reasons: (1) A contour map of the water table published by Murashita and others (1954) shows that the water table dips to the southeast. (2) The dip of the aquifer and the surface inclination of the plain accord with each other (figs. 1 and 2). (3) The

Oana (1954) suggested that it is feasible to deduce the time when water soaked into the ground by measuring the argon content of ground water. When water flows on the Earth's surface in contact with atmospheric air, its content of dissolved gases is determined by its temperature. The temperature of surface water varies seasonally, with a maximum in summer and a minimum in winter, and the content of dissolved gases therefore has a minimum in summer and a maximum in winter. When water soaks into a confined aquifer, its content of dissolved gases is expected to reflect the annual cycle of atmospheric

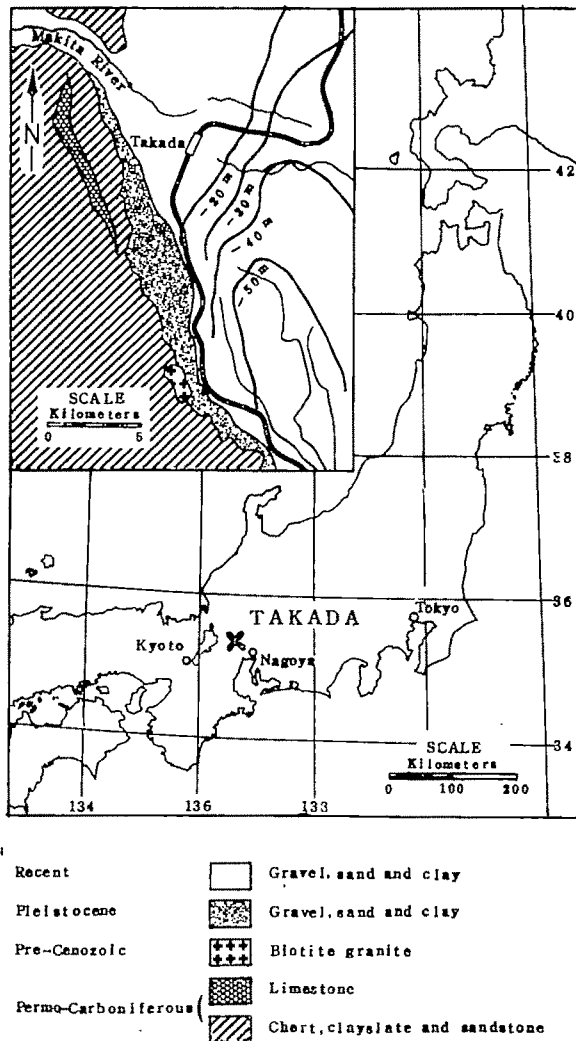


Fig. 1. Index map with geologic map of part of Nagoya District, based on 1:200,000 map published by the Geological Survey of Japan, 1955. On the geologic map, contour lines show the upper boundary of a gravel bed, the aquifer studied in this paper. Altitudes in meters below sealevel.

MEASUREMENT OF EFFECTIVE FLOW VELOCITY OF GROUND WATER BY MEANS OF DISSOLVED GASES

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ABSTRACT. Confined ground water is isolated from the air, and its content of dissolved gases is decisively controlled by the temperature of the water when it was exposed to the atmosphere. On account of seasonal variation of the original water temperature, there must be seasonal variation in the dissolved-gas content of ground water. The gas content as influenced by seasonal variation of temperature has been investigated by successive observations of water from a few wells and by simultaneous measurement of water from many wells. The time when water soaked into the ground can be inferred for each sample from the variation of dissolved-gas content, and the effective velocity of ground water can be calculated thereby. The effective velocity observed in an aquifer consisting of coarse gravel ranges from 3.6 to 10 meters per day, corresponding to different hydraulic gradients. If these values are converted by Darcy's formula into the velocity along a one percent hydraulic gradient, they range from 36 to 58 meters per day.

INTRODUCTION

In order to estimate the water-supplying ability of a well and of an aquifer, it is necessary to determine the coefficient of permeability in a stratum. There are several methods for determining the coefficient of permeability. One of these is to calculate it from the effective velocity of ground water in the field.

The earliest method used for measuring the velocity of ground water movement was that of Thiem (1887), who introduced sodium chloride in an upstream well and tested samples taken from a downstream well. The mean velocity was determined by the time elapsed until the highest chloride concentration occurred in the downstream well. Slichter (1905, p. 16-28) developed the method by using other electrolytes, and measured electrometrically. The conductivity of water is increased by the addition of an electrolyte; the variation of concentration of introduced ammonium chloride was electrically measured. Dyes such as uranin have also been used instead of salts. All these methods are widely used in the field. However, there are doubts about them: (1) When an appreciable amount of salt or dye solution is introduced in a well, the water level rises, increasing the inclination of the water table. (2) Dyes may sometimes be decomposed or absorbed by organic matter in the ground. (3) The salt or dye does not appear abruptly in the downstream well, but its appearance is gradual and irregular; it is difficult to determine the arrival time of the tracer.

It is therefore desirable to make use of natural tracers, which do not disturb the ground water table.

Grosse and others (1951) discovered the natural occurrence of tritium (half-life 12.5 yr) produced by cosmic rays. Libby (1959) measured the tritium content of water from selected wells in Nebraska and discussed its hydrologic application. Beryllium-7 produced by cosmic rays was also found in rainwater by Arnold and Al-Salih (1955). The half-life of Be^7 is only 53 days, and it would not be applicable to the study of ground water movement.

Part III of this series will describe the experimental studies on the melting relations of albite and granite in the presence of H_2O , together with HCl , P_2O_5 , SO_3 , and Li_2O .

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with HF solutions at 690°C, 730°C, and 760°C, where no feldspar remains. In each set of charges X-ray diffraction patterns demonstrate a proportional increase of quartz to HF content.

This effect may be caused or accentuated by preferential passage of alkali and alumina into the vapor phase, as in the system $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O--HF}$, leaving the liquid relatively enriched in silica. However, in this "system", X-ray diffraction patterns of the white crust deposited on the walls of the gold capsules reveal quartz as well as other phases developed in the albite system. There are also peaks with d spacings 5.68, 2.97, and 2.92; the first is prominent and the other two are weak. Two correspond to the peaks found for the vapor deposit in the albite system, but the relative intensities are reversed. The crust contains low index tabular crystals and isotropic spheres very similar to those described for the albite system.

DISCUSSION

Some applications of these results to petrological processes have been discussed elsewhere (Tuttle and Wyllie, 1957), and further applications will be reserved until data on the effect of other volatile materials have been presented. However, it should be pointed out at this stage that, in the systems described so far, the effect of the second volatile material (CO_2 , NH_3 , and HF) on the melting relations of granite has been similar to the effect on albite, confirming that the ternary systems $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O}$ —second volatile are satisfactory models for the complex "systems" granite- H_2O —second volatile.

The results described were obtained at constant pressure. In order to represent the effect of pressure in three dimensions, one of the other variables must be fixed, for instance, the composition. Since the temperature of beginning of melting is independent of the ratio of silicate to solution, we need fix only the concentration of the solution to illustrate as a curve the PT variation for the beginning of melting of a silicate in the presence of two volatile materials. At 2750 bars pressure the temperature of beginning of melting of granite in the presence of 4.3 weight percent HF solution is 605°C, 65°C lower than in the presence of H_2O alone. The PT curve for the beginning of melting of granite in the presence of 4.3 percent HF solution probably remains about 65°C below that for melting in the presence of H_2O alone, at least for pressures greater than 1000 bars. Similar PT curves will pass through each point on the solidus in the TX projection in figure 4.

The chemical reaction between albite and HF is a function of the ratio of HF to albite. For the fixed weight ratio of 1:1 silicate to total volatiles, the percentage of quartz developed in the system $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O--HF}$ increases with increasing HF concentration. However, for a given HF solution increase of the silicate:volatile ratio will decrease the ratio of HF to albite and the extent of reaction will also decrease. Therefore, for bulk compositions near the liquidus field boundary there is a strong possibility that quartz will not develop and that the phase relations may remain effectively ternary for solutions of much higher HF concentration. These conditions correspond more closely to magmatic conditions than the experiments described above, using a considerable excess of vapor.

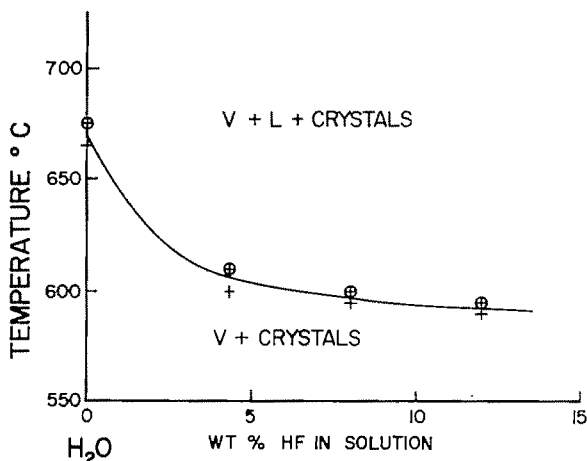


Fig. 4. Perspective TX projection for the "system" granite-H₂O-HF at 2750 bars pressure, determined for a 1:1 weight ratio (approximately) of granite to total volatiles. The curve is a projection of the solidus, and it shows the effect of HF in addition to H₂O, at constant pressure, on the temperature of beginning of melting of granite, compared to the effect of H₂O alone.

albite (in nonstoichiometric proportions) dissolved in the vapor phase was less than 2.9 weight percent.

Granite-H₂O-HF.—Six critical runs of 30 completed in this "system" are listed in table 2 and illustrated in figure 4. Granite behaves in the same manner as albite, i.e. the temperature of beginning of melting in the presence of excess vapor at constant pressure is lowered when the HF content of the charge is increased. Addition of a small percentage of HF produces a marked depression of the melting temperature, and further addition of HF produces a lesser effect; the curve for the beginning of melting begins to level off with increasing HF concentrations when the HF concentration reaches about 5 percent.

The lowering of the temperature of beginning of melting caused by addition of HF indicates that HF is more soluble in the liquid than is H₂O. In comparison with the model system NaAlSi₃O₈-H₂O-HF, the first liquid developed is richer in HF than is the bulk composition of the charge, i.e. the HF is more soluble in the liquid than H₂O. With increase in temperature for a given bulk composition, the feldspar passes into the liquid phase more readily than the quartz (established by optical and X-ray methods), and there is a wide temperature interval in which the charges consist of vapor + liquid + quartz + mica. Phase relations near the liquidus are not known for the "system" Westerly granite-H₂O, but from data on the system NaAlSi₃O₈-KAlSi₃O₈-SiO₂-H₂O (Tuttle and Bowen, 1958) and on the composition of this granite, the quartz should dissolve before the feldspar, leaving vapor + liquid + feldspar + mica (feldspar is the primary phase at this pressure).

Addition of HF to the "system" thus reduces the feldspar stability field relative to the quartz field. The feldspar is less stable in the presence of HF solutions than in the presence of H₂O, as would be expected, and the quartz appears to be more stable. This is suggested by the equilibrium assemblages

of glass. The refractive index of this material was somewhat lower than that of the glass developed by melting of albite. It appeared to be quite unrelated to melting, and it seems more likely that this is a gelatinous product resulting from the reaction between HF and albite. The material persisted above the solidus, but quartz was also enclosed in normal glass fragments, confirming that it was in equilibrium with the liquid. Occasionally, when glass was used as a starting material, large isolated albite crystals were partially surrounded by narrow envelopes of low index isotropic material. We have insufficient evidence to decide whether this is related to equilibrium conditions or whether it represents material deposited from the vapor phase during the quench.

Material precipitated from the vapor phase during the quench was far more abundant in this system than in $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ or $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-NH}_3$, indicating that much more solid material was dissolved in the vapor. The deposit from the vapor phase formed a white crust on the walls of the gold capsule, increasing proportionately with the concentration of HF. This crust could sometimes be collected and examined separately from the main charge.

Three phases were recognized in the deposit: (1) The low index isotropic spheres found sparsely scattered through the charges in other systems were abundant. In runs using 2 and 4.3 weight percent HF solutions the spheres were clear, but with the 8 percent solution a few minute birefringent crystals were present in the centers of the spheres. With the 12 percent solution the central crystals were so closely packed that they were opaque. The spheres, with black centers, occurred in large clusters. (2) Fragments and shreds of low index isotropic material with the appearance of glass. The refractive index of this and of the spheres was just below 1.476. (3) The third phase consisted of colorless crystalline material, possibly comprising at least two minerals. The crystals were of various sizes and habit, sometimes prismatic but more often tabular, with many crystal faces. They had low birefringence and very low refractive index (much lower than 1.476).

In several runs the amount of vapor deposit was great enough to yield X-ray diffraction patterns. In all patterns recorded three peaks appeared quite strongly with d spacings 2.92, 5.70, and 5.25, in order of decreasing intensity. We were unable to identify the crystalline material from these data. The development of free quartz in many runs suggests that Na_2O and Al_2O_3 passed into the vapor phase preferentially, and it seems probable that the crystals precipitated by the vapor phase during the quench consist of one or more sodium aluminum fluorides, possibly hydrated. The low refractive indices of such minerals tend to support this possibility. In the presence of H_2O alone at 500°C and pressures less than 2000 bars, Na_2O and SiO_2 pass into the vapor phase in excess of the albite ratio, leaving an excess of Al_2O_3 in the solid (Morey, 1957).

In two runs the vapor phase was separated from the solid and liquid phases using a technique which will be described in a later paper. Measurements were made to determine the weight percentage of the vapor phase precipitated as solid material during the quench. At 760°C , using the 4.3 weight percent HF solution, the two runs gave values of 2.9 and 3.0 weight percent. Some H_2O and HF were chemically bound in the solid, hence the amount of

The part of the system free of quartz (fig. 3) may be regarded as ternary, but even here it is unlikely that the compositions of liquids and vapors can be represented in terms of the three components. The significance of the upper curve can be understood by examining the melting behavior of a charge such as M in the system $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-NH}_3$ (fig. 2). In figure 2 and in the accompanying discussion, if HF were substituted for H_2O , and H_2O were substituted for NH_3 , the treatment and conclusions would be identical. Therefore, each point on the upper curve in figure 3 (when quartz is absent) represents equilibrium between a vapor on the projected vaporus field boundary (solidus) and a liquid on the liquidus field boundary, which is not shown. The vapor is poorer and the liquid is richer in HF than the bulk composition of the charge.

Because the addition of HF to H_2O at constant pressure lowers the melting temperature of albite compared to that in the presence of H_2O alone, we may conclude that the total molar percentage of volatiles dissolved in the silicate melt becomes greater as the concentration of HF in the volatile components is increased. Preliminary solubility measurements indicate that this is so; these results will be presented in a later paper, together with other solubility data.

Albite crystallized from glass in the presence of HF solutions is several times larger than that crystallized in the presence of H_2O alone. The crystals are well formed, with prismatic habit. They are of such a size that detailed optical measurements may be possible. X-ray powder diffraction patterns showed that the high-temperature form of albite crystallized in all runs. In the presence of H_2O , runs of very long duration (months) are required for the lattice parameters of high-temperature albite to approach the values characteristic of the temperature of crystallization (Mackenzie, 1957). From a few trial runs it appears that addition of HF does not appreciably affect the rate of structural change despite the fact that HF is such an effective flux in the liquid phase.

The runs containing quartz lie to the right of the dashed line in figure 3. In general the amount of quartz increases with HF concentration and decreases with increasing liquid content. No quartz could be found in charges using 2 weight percent HF solution, and most quartz was developed in subsolidus runs using the 12 percent solution. Here, quartz constituted about 20 percent of a charge. In all runs above 640°C only a few percent quartz was present, barely sufficient to be detected by X-ray diffraction patterns. Thus, only a trace of quartz persisted above the stability field of albite. Several runs were completed between 580°C and 700°C , using a 20 weight percent HF solution. Albite had no stability field at this concentration, pressure and temperature range, quartz being the only stable crystalline phase.

The quartz crystallized as short hexagonal prisms doubly terminated by pyramids. The prism faces were always subordinate to the pyramids and were often absent altogether. This is the characteristic habit of β (high) quartz. No change could be detected in the habit of the quartz in the temperature interval 580°C to 710°C . According to Yoder (1950), the $\alpha \rightleftharpoons \beta$ quartz inversion of this pressure occurs at 645°C .

In subsolidus runs the quartz crystals occurred singly or in clusters, and they were usually enclosed by low index isotropic material with the appearance

TABLE 2

Results of quenching experiments in the system $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O--HF}$
and the "system" granite- $\text{H}_2\text{O--HF}$. Pressure: 2750 bars

Initial Silicate Material	Weight Percent Silicate	Temp. °C	Time Hours	Result
NaAlSi ₃ O ₈ —2 weight percent HF solution				
crystalline	ca.50*	650	18	V + Ab
crystalline	ca.50	675	21	V + L + Ab
glass	57	780	29	V + L
NaAlSi ₃ O ₈ —4.3 weight percent HF solution				
crystalline	ca.50	630	20	V + Ab + Qz**
crystalline	ca.50	650	18	V + L + Ab
glass	52	705	19	V + L + Ab
glass	50	720	19	V + L
NaAlSi ₃ O ₈ —8 weight percent HF solution				
crystalline	ca.50	600	22	V + Ab + Qz
crystalline	ca.50	615	312	V + L + Ab + Qz
glass	50	680	20	V + L + Ab + Qz
glass	50	690	18	V + L + Qz
glass	50	705	19	V + L
NaAlSi ₃ O ₈ —12 weight percent HF solution				
crystalline	ca.50	590	23	V + Ab + Qz
crystalline	ca.50	600	22	V + L + Ab + Qz
glass	51	630	26	V + L + Ab + Qz
glass	51	650	18	V + L + Qz
glass	55	720	19	V + L + Qz
Granite—4.3 weight percent HF solution				
crystalline	ca.50	600	6	V + crystals
crystalline	ca.50	610	2	V + L + crystals
Granite—8 weight percent HF solution				
crystalline	ca.50	595	392	V + crystals
crystalline	ca.50	600	25	V + L + crystals
Granite—12 weight percent HF solution				
crystalline	ca.50	590	28	V + crystals
crystalline	ca.50	595	28	V + L + crystals

* Between 40 and 60 weight percent. The proportions were estimated for solidus measurements.

** Qz = quartz.

If the system were not complicated by reaction, the lower curve in figure 3 would represent a projection of the vaporus field boundary $V(L + Ab)$, and the upper curve a projection of the liquidus for compositions with a 1:1 weight ratio of silicate to total volatiles. In fact, the lower curve is a projection of the solidus for the system while the upper curve represents the upper stability limit of albite for these compositions. The latter is not a projection of the liquidus because quartz is stable to higher temperatures for the higher HF concentrations.

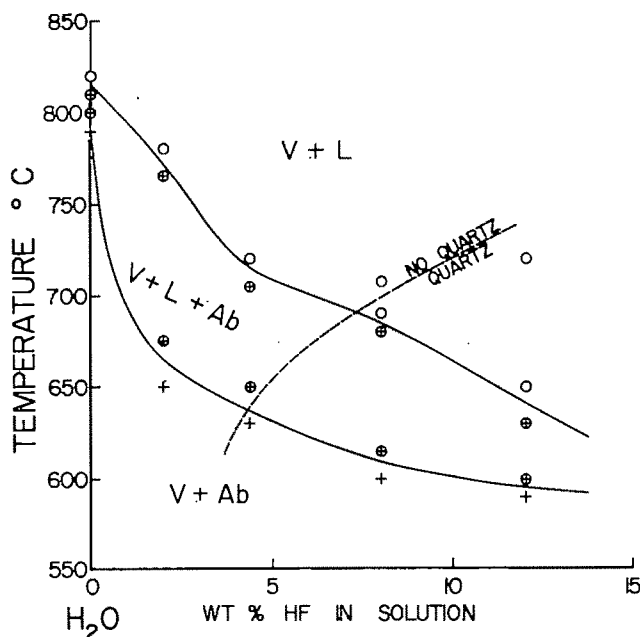


Fig. 3. Perspective TX projection for the system $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-HF}$ at 2750 bars pressure, determined for a 1:1 weight ratio of $\text{NaAlSi}_3\text{O}_8$ to total volatiles. The lower curve is a projection of the solidus, and the upper curve is a projection of the upper stability limit of albite for these compositions. Quartz is stable to the right of the dashed line, and here the system is no longer ternary. Only a trace of quartz is present above the upper curve.

projections from isobaric multicomponent space, and comparison with the ternary models derived in Part I should be made with caution. However, the plotted curves appear to be indicative of a minimum on the field boundaries for some concentration of HF greater than 12 weight percent (figs. 6D, 7D, and 10 in Part I).

Because temperatures involved in this system are lower than in $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-NH}_3$, longer runs were possible, and it was not difficult to establish equilibrium. Many more runs were completed than those listed in table 2, and many duplicate runs were made using glass and crystalline starting materials. Several runs of much longer duration were completed to check equilibrium. The same results were obtained in 312 hrs as in 18 hrs.

In the systems $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ and $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-NH}_3$ the temperature of beginning of melting was readily determined by the appearance of glass of low refractive index. In the system $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-HF}$ the situation was complicated to some extent by the precipitation of low index phases from the vapor during the quench. In some runs below the solidus of figure 3 there appeared to be a trace of glass locally developed, but for a given bulk composition the solidus was taken as the temperature at which a small amount of glass developed uniformly throughout the charge; above this temperature the proportion of glass developed increased regularly.

higher temperature than T_2 ; if the ratio is less than 1:1, it will occur at a lower temperature.

The $V + L(\text{Ab})$ side of the three-phase triangles generates the ruled surface $V + L(\text{Ab})$, and the temperature of complete melting for any charge with bulk composition between the two field boundaries is thus the temperature at which a vertical line through the bulk composition intersects the $V + L(\text{Ab})$ surface. The point M' in figure 2B is a projection of the point of intersection with this surface of a vertical line through M , and the dotted line $E'M'F'$ in figure 2B represents the intersection of a vertical plane through EF (fig. 2A) with the surface $V + L(\text{Ab})$. The experimentally determined upper curved line in figure 1 thus corresponds to the dotted line $E'M'F'$ in figure 2B.

Each point on this curve represents equilibrium between a vapor on the projected vaporus field boundary and a liquid on the liquidus field boundary, which is not shown. The vapor is richer and the liquid is poorer in NH_3 than the bulk composition of the charge. For a given volatile composition in figure 1, the liquidus field boundary projects at a higher temperature than the upper curved line (compare with fig. 2B).

Field boundaries in the system could exhibit a maximum for some concentration of NH_3 greater than 25 weight percent (see figs. 6C and 7C, Part I), but for that portion of the system with field boundaries ascendant from $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ (as in fig. 1) charges would behave in the manner described above.

Because addition of NH_3 to H_2O raises the melting temperature compared to that in the presence of H_2O alone, we may conclude that the total molar percentage of volatiles dissolved in the silicate melt becomes smaller as the concentration of NH_3 in the volatile components is increased.

Albite crystallized from glass in the presence of NH_3 solutions appeared identical with that crystallized in the presence of H_2O . Products were examined both optically and with an X-ray diffractometer, but no detailed structural studies were made. The high-temperature form of albite was found in all runs (Mackenzie, 1957).

Only one point was determined on the solidus of the "system" granite- $\text{H}_2\text{O-NH}_3$. The critical runs are listed in table 1. Using a charge with approximately 50 weight percent granite and a solution containing 8.2 weight percent NH_3 , the temperature of beginning of melting at 2750 bars pressure lies between 680°C and 700°C . In the presence of H_2O alone at the same pressure, the temperature of beginning of melting is $670^\circ\text{C} \pm 5^\circ\text{C}$. Granite therefore behaves in the same manner as albite; the melting temperature in the presence of excess vapor is raised when the proportion of NH_3 in the vapor is increased at constant pressure.

$\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-HF}$.—The critical runs at 2750 bars pressure (listed in tables 1 and 2 and illustrated in fig. 3) show that the addition of HF to H_2O at constant pressure lowers considerably the melting temperature of albite when compared with its melting temperature in the presence of H_2O alone. The system is not ternary because extensive chemical reaction occurs between HF and albite. Quartz appears as a stable phase when the concentration of HF in the aqueous solution exceeds 4 weight percent. The curves in figure 1 are thus

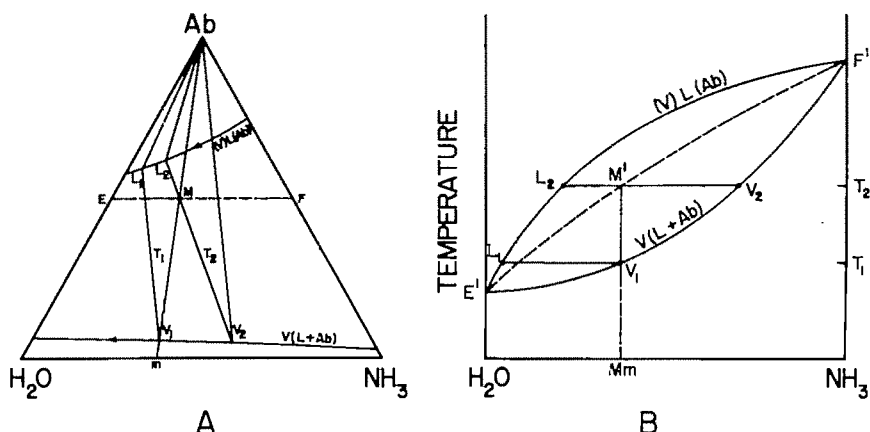


Fig. 2. Schematic isobaric polythermal projection (A) and perspective TX projection (B) of the system $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-NH}_3$, illustrating the melting behavior of the charge M, which contains 50 weight percent $\text{NaAlSi}_3\text{O}_8$ and 50 percent solution m . The solidus and liquidus temperatures for this charge are T_1 and T_2 . Three-phase triangles, AbL_1V_1 and AbL_2V_2 , are shown for these temperatures. The dashed line E'M'F' in figure 2B corresponds to the upper curve in figure 1.

figure 2 illustrates schematically their arrangement in the isobaric polythermal equilibrium diagram (fig. 2A) and in the perspective TX projection (fig. 2B). Two isothermal three-phase triangles are shown in each projection. The triangles $\text{V}_1\text{L}_1\text{Ab}$ and $\text{V}_2\text{L}_2\text{Ab}$ in figure 2A, at temperatures T_1 and T_2 , appear in figure 2B as horizontal straight lines, V_1L_1 and V_2L_2 , connecting pairs of points on the projected field boundaries. The line EF in figure 2A represents the 1:1 weight ratio line, giving the bulk compositions of the charges used to determine the upper curve in figure 1. Consider the charge with bulk composition M, consisting of 50 weight percent albite and 50 weight percent NH_3 solution with concentration m . The two three-phase triangles were chosen so that the sides V_1Ab and V_2L_2 intersect (in projection only) at M.

When M is heated in a closed system, it consists of $\text{V} + \text{Ab}$ until it reaches temperature T_1 when the vapor composition is V_1 on the vaporus field boundary. At T_1 , M is about to enter the three-phase triangle $\text{V}_1\text{L}_1\text{Ab}$, and a trace of liquid L_1 develops. Note that this occurs wherever M may lie on the line V_1Ab , i.e. for a charge containing a solution of a given composition, m , the temperature of beginning of melting is independent of the ratio of silicate to solution (total volatiles). Between the temperatures T_1 and T_2 , the charge M lies within the three-phase space $\text{V} + \text{L} + \text{Ab}$, and the compositions of the vapor and liquid change along the vaporus field boundary from V_1 to V_2 and along the liquidus field boundary from L_1 to L_2 . At T_2 the last trace of albite melts, and the charge consists of $\text{V}_2 + \text{L}_2$. At temperatures greater than T_2 the charge lies within the two-phase space $\text{V} + \text{L}$.

The temperature of complete melting is the temperature at which the $\text{V} + \text{L}(\text{Ab})$ side of a three-phase triangle passes through the bulk composition of the charge. Note that for a charge containing a solution of a given composition, m , if the silicate:solution ratio is greater than 1:1, this will occur at a

However, there appears to be little doubt concerning the equilibrium assemblage. Many more runs were completed than those listed in table 1, and duplicate runs were frequently made using glass and crystalline material. Crystalline material was used for determination of the beginning of melting because a trace of glass is readily detected optically, whereas glass was used as a starting material for determination of the liquidus because the growth of a few crystals in glass is sufficient to indicate the "direction" of equilibrium.

When held one hour in the field $V + L$ (fig. 1), crystalline material (with either pure H_2O or NH_3 solutions) was not completely melted. The charge consisted of a white raft of crystals surrounded by a border of glass, the thickness of which increased with the duration of the run. Under the same conditions no albite grew in a charge containing glass as a starting material. Crystalline material, if held in the field $V + L + Ab$ in figure 1, was converted to a white raft of crystals surrounded by a translucent glass border containing dispersed albite crystals. With glass as a starting material, the product consisted of a translucent glass bead with albite crystals spread evenly throughout.

When crystals were used as a starting material, the phases present in the border, which developed around the raft of remnant albite, correspond to the phases produced when glass was used as a starting material. This is therefore believed to be the equilibrium assemblage although the albite and glass may not be in equilibrium proportions. If the runs could have been continued for a longer time, the remnant albite would probably have been converted to the material preserved in the border zone.

Melting undoubtedly began where vapor was in contact with the charge, and development of a zone of liquid around the crystals appeared to protect them from further melting until the vapor had time to diffuse through the outer zone. On the other hand, with glass as a starting material, nucleation of crystals in the presence of excess vapor appeared to proceed quite readily, although we do not know the length of time required for the attainment of equilibrium.

The results listed in table 1 show the equilibrium assemblages interpreted from the listed runs and from duplicate runs. Excess vapor was present in all charges, and microscopic examination revealed a few of the low index isotropic spheres characteristically precipitated during the quench from the vapor phase in silicate-water systems. The amount of albite dissolved in the vapor phase is not known.

The lower curve in figure 1, the temperature of beginning of melting, coincides with the projection of the vaporus field boundary $V(L + Ab)$,¹ but the upper curve, giving the temperature of complete melting, is the liquidus curve for charges containing a 1:1 weight ratio of albite to total volatiles. It is *not* a projection of the liquidus field boundary $(V)L(Ab)$, as are the similar curves in figure 6, Part I. The significance of the upper curve can most readily be explained by examining the melting behavior of a charge containing this ratio of albite to total volatiles.

Let us assume first that there is no maximum on the field boundaries, then

¹ See Part I for key to abbreviations.

TABLE 1

Results of quenching experiments in the system $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O--NH}_3$ and the "system" granite- $\text{H}_2\text{O--NH}_3$. Pressure: 2750 bars

$\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O}$				
Initial Silicate Material	Weight Percent Silicate	Temp. °C	Time Hours	Result
crystalline	ca.50*	795	3.00	V + Ab
crystalline	ca.50	800	2.25	V + L + Ab
glass	ca.50	805	2.50	V + L + Ab
crystalline	ca.50	810	2.00	V + L
$\text{NaAlSi}_3\text{O}_8\text{--1.75 weight percent NH}_3\text{ solution}$				
crystalline	51	795	3.00	V + Ab
crystalline	52	800	2.25	V + L + Ab
glass	48	810	2.00	V + L + Ab
glass	50	815	2.00	V + L
$\text{NaAlSi}_3\text{O}_8\text{--3.75 weight percent NH}_3\text{ solution}$				
crystalline	49.5	795	3.00	V + Ab
crystalline	ca.50	800	2.25	V + L + Ab
crystalline	53.0	810	2.00	V + L + Ab
glass	50.0	820	1.50	V + L
$\text{NaAlSi}_3\text{O}_8\text{--8.2 weight percent NH}_3\text{ solution}$				
crystalline	49.5	800	2.25	V + Ab
crystalline	48.0	810	2.00	V + L + Ab
crystalline	50.5	820	1.75	V + L + Ab
glass	52.0	830	2.25	V + L
$\text{NaAlSi}_3\text{O}_8\text{--22.5 weight percent NH}_3\text{ solution}$				
crystalline	49.0	820	2.25	V + Ab
crystalline	ca.50	830	2.50	V + L + Ab
crystalline	52.0	850	1.00	V + L + Ab
glass	50.0	860	1.00	V + L
Granite- H_2O				
crystalline	ca.50	665	24.0	V + crystals
crystalline	ca.50	675	24.0	V + L + crystals
Granite-8.2 weight percent NH_3 solution				
crystalline	ca.50	680	48.5	V + crystals
crystalline	ca.50	700	22.5	V + L + crystals

* Ca.50: Between 40 and 60 weight percent. The proportions were estimated for solidus measurements.

of impurity affects the liquidus temperature only slightly, and the melting temperature is normally taken as that at which the last crystal disappears. A more reasonable representation of the phase relationships would therefore be given if the lower curve in figure 1 were moved upwards through 10°C until it meets the upper curve on the H_2O axis.

Because of the relatively high temperatures involved, all runs were of short duration (from one to three hours), and equilibrium was not attained.

coexisting with silicate liquids and crystalline material is thus a fluid phase which can be transformed continuously into vapor of liquid by suitable variation of P , T , and X . The nature of this phase was discussed in Part I and hereafter it will be called a vapor to distinguish it clearly from the silicate liquid phase.

Although nitrogen is apparently unimportant in magmatic systems, the system $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O--NH}_3$ is described first. It was selected as the most suitable to illustrate the principles outlined in Part I because chemical reaction between albite and NH_3 solutions could not be detected. The second system, $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O--HF}$, has direct bearing on crustal melting and magmatic processes, but it is complicated by chemical reaction between HF and albite.

$\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O--NH}_3$.—The critical runs at 2750 bars pressure, listed in table 1 and illustrated in figure 1, show that the addition of NH_3 to H_2O at constant pressure raises the melting temperature of albite. This system is therefore either of the type illustrated in figures 5, 6A, 7A, and 8 in Part I, or possibly one with a maximum on the field boundaries, figures 6C, 7C, and 9 in Part I.

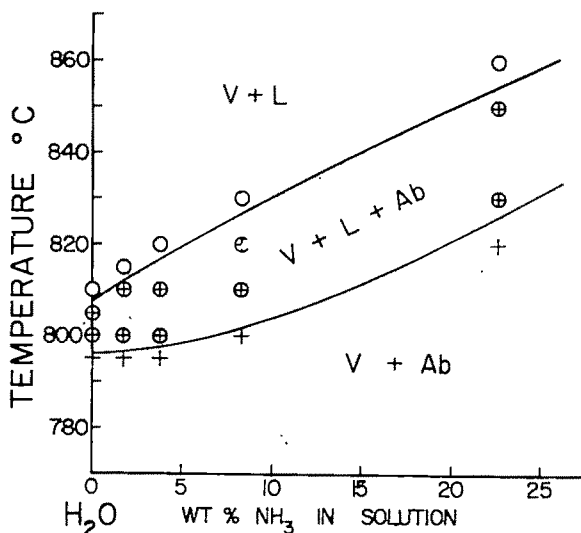


Fig. 1. Perspective TX projection for the system $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O--NH}_3$ at 2750 bars pressure, determined for a 1:1 weight ratio of $\text{NaAlSi}_3\text{O}_8$ to total volatiles. The lower curve is a projection of the vaporous field boundary, $V(L + Ab)$, and the upper curve is the liquidus for these compositions. The liquidus field boundary would project at a higher temperature than the upper curve (see fig. 2B).

The axis above the H_2O composition is a projection of the isobaric section in the system $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O}$. Theoretically, albite should melt directly to a liquid in the presence of excess water vapor at constant pressure but, in fact, there is a melting interval of about 10°C . However carefully a silicate mineral may be prepared, it would be fortuitous if it were exactly on composition, and even the purest of synthetic minerals will exhibit a melting interval. Greig (1927) and Yoder (1952) have discussed this matter in some detail. A trace

ponent. There is such a great difference between the physical and chemical properties of the volatile materials on the one hand, and of the albite or granite on the other, that it seems not unreasonable to regard the granite and the crystalline assemblages appearing under different conditions as one "silicate component" in a "ternary" system containing two volatile components. The TX projections permit us to see the effect of the second volatile component, in addition to H_2O at fixed pressure, compared to the effect of H_2O alone.

In all the systems studied, attention was first concentrated on charges containing 50 percent (by weight) of the silicate. From figure 5C in Part I, it is clear that for a given concentration of an aqueous solution the temperature of beginning of melting is not affected by the ratio of silicate to solution (total volatiles), but the liquidus temperature can vary considerably with this ratio. Charges for liquidus measurements were therefore weighed out carefully, whereas for solidus measurements the weights were estimated. With practice it is not difficult to keep the ratio of silicate to solution within the limits of 40 to 60 weight percent without weighing. Measurements near the liquidus field boundary and within the vapor-deficient region will be described in later papers, after the effects of the various volatile materials on the solidus have been detailed.

The systems containing albite, H_2O , and a second volatile have been treated as ternary, although the state of the volatile components within the sealed capsules is not known. For instance, in the system $NaAlSi_3O_8-H_2O-NH_3$, some or all of the following constituents could be present: H_2O , H_2 , O_2 , H^+ , OH^- , NH_3 , N_2 , NH_4OH , and NH_4^+ . However, if we attempted to consider the products of reaction between the volatile materials as separate components, the treatment would become hopelessly involved. H_2O is regarded as a single component in hydrothermal systems, although some dissociation undoubtedly occurs at elevated temperatures. The results obtained in this system are readily understood if the composition NH_3 is taken as the third component, and similar arguments apply to other systems.

The silicate phases do not react with H_2O in the experimental PT range, but in most systems studied some chemical reaction does occur with the second volatile material. With increasing concentration of the second volatile, the reaction may increase to such an extent that it cannot be neglected. For instance, in the system $NaAlSi_3O_8-H_2O-HF$, quartz crystallizes when the amount of HF in the aqueous solution added to albite exceeds 4 weight percent (with 50 percent total volatile). Although the system can no longer be regarded as ternary, it is convenient to plot the results as though it remained ternary, and this procedure is followed below.

An isobaric section at 2750 bars through the PTX model for the system $NaAlSi_3O_8-H_2O$ lies between the first and second critical end-points (see Part I), and this is also probably true for many of the systems $NaAlSi_3O_8$ -second volatile. However, addition of the second volatile may lead to the intersection of critical curves and surfaces in the isobaric prism, but since we are dealing experimentally with quite low concentrations of the second volatile, this is unlikely to occur within the PTX range of the present studies. The aqueous phase

was lowered over the pressure vessel containing the sealed capsules, and, when the required pressure developed, it was maintained at this level by bleeding the system through a valve. The walls of the capsules collapsed in response to the external pressure, which was thus transmitted to the liquid and vapor phases within. At the end of a run the furnace was raised from the pressure vessel, which was quenched by a blast of compressed air; the quench was sufficiently rapid to freeze the equilibrium in the silicate melt. The pressure was not released until the charges were cool enough to insure that the capsules would not expand and burst. After comparing the weight of a sealed capsule with its weight before the run to make sure that there had been no leakage, the capsule was cut open. The charges were dried, crushed, and examined using an X-ray diffractometer, and in immersion media using a petrographic microscope.

Pressure measurements are believed to be accurate to 3 percent, and temperature measurements to $\pm 5^\circ\text{C}$. When runs at close temperature intervals were required to locate boundaries, as in the system $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O--NH}_3$ (fig. 1), the critical points were determined by holding a series of four charges in the same pressure vessel at a fixed pressure and temperature. For example, charges containing albite plus (1) H_2O , (2) 1.75 percent NH_3 , (3) 3.75 percent NH_3 , and (4) 8.2 percent NH_3 solutions were held at 800°C in the same pressure vessel at the same time (fig. 1, table 1). Melting was observed in three charges, but not in the fourth. A similar run at 795°C revealed no melting in any of the charges. The temperature measurement is not sufficiently accurate to locate the boundary if all these points had been determined in separate runs in different pressure vessels, but the method used fixes the relative position of the boundary.

RESULTS

General remarks.—In order to represent a ternary system in three dimensions, one of the variables, pressure, temperature, and composition, must be fixed. Since it is convenient experimentally to work under isobaric conditions, we fixed the pressure, and most of the results were obtained at a constant pressure of 2750 bars. This corresponds to a depth of 11.2 km in the Earth's crust, assuming a cover of sediments with an average density of 2.5.

The complete representation of phase relations in molecular or weight percentages differs considerably for systems containing both silicates and volatiles, and molecular percentages were used exclusively in Part I. However, weight percentages are more familiar when we think of natural rocks, and these will be used to present the results. Most of the results are illustrated in perspective TX projections from within isobaric prisms onto the faces representing volatile components of the prisms. These diagrams show the proportions of the two volatile components in liquids and vapors without showing the proportion of silicate, and plotting them in molecular or weight percentages would make little difference. Later in this series, when the effects of the different volatiles are compared, the results will be converted into molecular percentages in order to facilitate structural interpretation of the data.

Results for the "systems" granite plus two volatiles have been plotted in the same way by treating the granite as though it were a single silicate com-

granite. Results are presented in perspective TX projections from within isobaric TX prisms, and familiarity with Part I is required for complete comprehension of the diagrams.

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EXPERIMENTAL METHOD

Starting materials.—The silicates used were: (1) Synthetic albite glass, (2) albite crystallized hydrothermally from the glass, (3) natural granite (Westerly, Rhode Island), and (4) homogeneous glass prepared by repeated fusion of the granite. The albite glass was prepared using the method described in detail by Schairer and Bowen (1956), and crystalline albite was prepared in large sealed gold capsules using the method described by Mackenzie (1957). The Westerly is a plagioclase-microcline-quartz granite, with biotite and muscovite; its chemical, normative, and modal compositions are tabulated by Tuttle and Bowen (1958, table 11).

Solutions of NH_3 with required concentrations were prepared from distilled H_2O and "Baker Analyzed" ammonia. Their compositions were checked by titration against standardized HCl solutions, and they were stored in a cool place in tightly stoppered bottles to minimize NH_3 loss by evaporation. After completion of the runs, the solutions were checked again by titration, and the averages of concentrations before and after the experiments were taken as the true values. The solutions of HF were prepared from distilled H_2O and "Baker Analyzed" concentration hydrogen fluoride. The ingredients were mixed in the appropriate volumetric proportions to give solutions of the required concentrations, and these were stored in a cool place in tightly stoppered polyethylene bottles to minimize evaporation losses. These solutions were not standardized, but they are believed to be accurate to within 0.5 weight percent HF .

Equipment and method.—Charges were sealed inside gold capsules 15 mm long, with 2.5 mm internal diameter and 0.1 mm wall thickness. Gold tubes were cleaned with pipe cleaners, then soaked thoroughly in dilute HCl and washed in several changes of distilled water. One end of the tube was welded shut in a carbon arc and an aqueous solution of NH_3 or HF of known concentration was pipetted into the tube. The required weight of the silicate starting material was added, and the open end of the tube was sealed temporarily in the jaws of a vise to insure that no volatiles escaped during final welding in the carbon arc. The welding method has been described in detail by Tuttle and England (1955). The weights of solution and silicate within the sealed capsule were obtained by subtraction. This method provides a small closed system containing three components in the required proportions (up to the limit of solubility of the second volatile in H_2O) which can be maintained at constant pressure and temperature until equilibrium is attained.

All runs were made in cold-seal pressure vessels (Tuttle, 1949) which were heated externally by nichrome furnaces (see also Harker and Tuttle, 1955). Temperatures were controlled by galvanometer-type controllers. Pressures were applied to the capsules by pumping water into the system with an air-operated pump. Pressures were measured by Bourdon gauges. The furnace

EXPERIMENTAL INVESTIGATION OF SILICATE SYSTEMS CONTAINING TWO VOLATILE COMPONENTS

PART II. The Effects of NH_3 and HF , in Addition to H_2O on the Melting Temperatures of Albite and Granite*

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ABSTRACT. Addition of NH_3 to water-albite and water-granite mixtures at constant pressure raises the melting temperatures of albite and granite, whereas addition of HF to these mixtures causes marked lowering of melting temperatures. Results obtained at 2750 bars pressure for charges containing 1:1 weight ratio of silicate to total volatiles are presented as perspective TX projections from within isobaric prisms onto the volatile faces of the prisms. In the presence of H_2O alone at 2750 bars pressure, albite melts between 795°C and 810°C, and granite begins to melt at 670°C; in the presence of 8.2 weight percent NH_3 solution, the melting interval of albite is 805°C to 825°C, and granite begins to melt at 690°C; in the presence of 8 weight percent HF solution, the melting interval of albite is 610°C to 685°C, and granite begins to melt at 595°C. No chemical reaction was detected in systems containing NH_3 , but considerable reaction occurs with HF . With increasing HF concentration in the system $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-HF}$, quartz becomes a stable phase and the system is no longer ternary. In the presence of HF solutions, albite crystals grow much larger than in the presence of H_2O alone.

INTRODUCTION

This is the second in a series of papers describing the effects of volatile materials, in addition to water, on the melting temperatures of rock-forming silicates. In this study we are primarily interested in the melting relations of granite, and we have therefore investigated a series of "systems" granite- H_2O -second volatile. As a basis for interpreting the results obtained in these complex systems, we have also investigated a series of systems $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ -second volatile. These can be treated as ternary systems, at least for low concentrations of the second volatile and the results can be presented in simple phase diagrams.

In Part I (Wyllie and Tuttle, 1960) we described the phase relations in ternary "systems" $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ -second volatile. The treatment was geometrical, and its purpose was to give a three-dimensional picture of the phase spaces, surfaces, and lines within ternary isobaric (TX) prisms for such systems. Three possible arrangements of the liquidus and vaporus field boundaries between the bounding binary systems $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ and $\text{NaAlSi}_3\text{O}_8\text{-C}$, where C is a second volatile component, were described: (1) They pass continuously in temperature and composition from one binary system to the other, (2) they have a temperature maximum, and (3) they have a temperature minimum. Previously published data on the effects of CO_2 and H_2O on the melting temperatures of feldspars and granite (Wyllie and Tuttle, 1959) were compared with the theoretical models. This paper describes the effects of NH_3 and HF , in addition to H_2O , on the melting temperatures of albite and

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Concerning question three, Salmi found that only very small amounts of trace elements were absorbed by laboratory monkeys in the process of digestion. This led him to conclude that absence of an element in the feces can be interpreted as absence of the same element in the food. However, Underwood (1956) has shown that under conditions of deficiency selective concentration of minerals can occur. Animals and man may absorb up to 90% of certain trace elements in their diets. Even in high quality diets man absorbs 73 to 97% of the cobalt ingested, eliminating about 14% in the feces and an average of 67% in the urine. If *Nothotherium* depended upon cobalt, it probably absorbed most of that available and eliminated only a few percent, which would be undetectable with instruments of 1 ppm sensitivity limit. More sensitive techniques (neutron activation) must be applied to this problem. But there is no evidence that sloths ever depended upon cobalt or copper to a greater extent than other non-ruminants, which are quite independent of these two elements.

It appears that neither the stratigraphic record at Rampart Cave nor our knowledge of deficiency diseases indicate copper-cobalt shortage as a possible cause of sloth extinction.

The Durable Mystery

Taking stock of the fossil and ecological record we note the following: (1) *Nothotherium shastense* browsed on a variety of xeric and semixerix Southwestern shrubs; its South American relatives lived in a tropical environment. (2) The chronology of extinction indicates that most ground sloths survived the glacial period into early postglacial time. (3) The Pliocene radiation of Pilosa northward into North America, their diversified browsing habits in both forest, savanna, and desert, and their wide range through a variety of climatic zones do not suggest overspecialization, senescence, or vulnerability to environmental stress.

The interesting suggestion of Salmi that copper and cobalt deficiency will account for the extinction phenomenon is unsupported by trace element analysis of *Nothotherium* dung in Rampart Cave.

We conclude that, despite their apparent clumsy build and bizarre morphology, the Pilosa were occupying a very important ecological role—one to which most other mammalian herbivores were less perfectly adapted. We are unable to identify a superior large browsing mammal that might have replaced *Nothotherium* in postglacial time. Its niche as a desert herbivore remains unfilled today. On all biological evidence this sloth should have survived into historic times.

In the Late Pleistocene the archaeological record shows that man and sloth were contemporaneous, a circumstance inconclusive in itself. Nevertheless, extinction might become understandable if Early Man were identified as the main cause. We find no other.

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In brief, the ecology of living gravigrades reveals no clues to explain extinction of the ground sloths.

Trace Elements and Extinction

Salmi (1955) has proposed that trace element deficiency, induced by drought in Late-glacial time, triggered the demise of *Mylodon* and other sloths. He found the amount of certain elements (copper, selenium, cobalt, silver) to be lower in the feces of *Mylodon* than in that of certain animals investigated in Finland (laboratory rhesus monkeys, native *Alces* and *Lepus*). In dung from South American caves, he detected about one-tenth the copper found in feces of the Finnish animals. Monkeys fed bread, carrots, and potatoes with an ash content of about 5% voided feces with an ash content of about 20%. The proportions of most trace elements increased in about the same ratio as did the ash content. Depletion of trace elements during digestion was slight. To Salmi the pronounced low values for certain elements in sloth feces seemed to indicate their scarcity in the food ingested by these animals. On this basis he concluded that the diet of *Mylodon* was critically deficient in cobalt, copper, and possibly other elements.

Salmi's experimental methods and conclusion raise interesting questions:

- (1) Are trace element diseases important in limiting populations of animals?
- (2) Are native as opposed to introduced species affected?
- (3) Are feces adequate indicators of dietary deficiency?

With regard to the first, deficiency diseases in domestic ruminants are well known (Orr, 1929; Russell, 1944; Stiles, 1946; Underwood, 1956). Ruminants require cobalt to enable bacteria of the rumen to synthesize vitamin B₁₂, which contains this element. Most cases of copper and cobalt deficiency occur in Africa, Australia, and New Zealand where stock raising was developed with the introduction of fastgrowing European breeds. These have higher mineral requirements than the native herbivores. Attempts to induce copper-cobalt deficiency diseases in animals other than ruminants have failed. Rats and rabbits reared and maintained on a deficient diet for several generations gave no indication of abnormality (Tompsett, 1940; Underwood, 1956).

Regarding the second question, our literature search unearthed no examples of copper-cobalt deficiency disease limiting native herbivores in their natural habitat. Such examples must appear before any such hypotheses can be advanced.

It is known that animals living under deficient soil conditions seek food of high mineral content and, if necessary, are able to supply themselves with minerals directly from the ground (Orr, 1929). If sheep afflicted with copper-cobalt deficiency are removed to a plowed field in an area where the deficiency does not occur, they will recover themselves, even though they are fed grass cut and transported from their old pasture (McNaught and Paul, 1939). On poor pastures with low mineral content the forage selected by animals is richer in minerals than that left uneaten (Orr, 1929).

In their native environment and on an open range it would appear extremely unlikely that large herbivores would fail to fill their mineral requirements under any geoclimatic circumstances.

Large diurnal grassland herbivores such as horses and artiodactyls generally require a water supply independent of their food source. On the other hand, many of the more successful of the desert herbivores are dependent only on metabolic water and evade thermal stress by nocturnalism, burrowing habits, and other behavioral adaptations. It seems quite likely that some of these adaptive features were shared by *Nothotherium*, which could have derived most of its water from cactus, yucca, and other succulents, and perhaps sought refuge in caves or rock shelters in the day. The nature of dung in Rampart Cave indicates no leaching by urine.

Gregariousness is highly developed in most large cursorial herbivores inhabiting savannas, grassland, or tundra. In evading predators and protecting young such behavior has an adaptive advantage. On the basis of its morphology and fossil record it appears that *Nothotherium* was solitary. In captivity tree sloths are decidedly antisocial (Beebe, 1926; Britton, 1941; Enders, 1935). According to Cabrera and Yepes (1940) the anteaters tend to be solitary except in the mating season or when the females are carrying their single young.

Although tree sloths can scarcely be considered gregarious, they do have certain remarkable social behavior. In a park at Santos, Krieg (1939) observed that four three-toed sloths used a common dung midden, climbing down from their trees to defecate in turn. He was unable to explain this behavior, which resembles that of the vicuna and guanaco. If *Nothotherium* voided in similar fashion, it is likely that the dung deposits in Rampart Cave grew as isolated midden mounds. In such event the stratigraphic sequence in one part of the cave would not be comparable to that elsewhere.

In tree sloths the passage of food through the digestive tract is extremely slow. Britton (1941, p. 32) reported the stomach contents may exceed 25% of the body weight. Food remains in the stomach 70 to 90 hours and requires a week to traverse the alimentary canal (Britton, 1941; Enders, 1940). The anteater *Tamandua* stores fecal material before defecation; a peculiar fecal sheath may prevent absorption of decomposition products (Enders, 1935, p. 494). Possibly the hardened mucus varnish enclosing *Nothotherium* dung (Laudermilk and Munz, 1934) had a similar function. Both the dry nature of sloth feces, commented on by Krieg, and the mucus sheath reduce the chance of leaching and chemical alteration between strata after deposition.

One aspect of sloth ecology neglected by most authors is the *raison d'être* of its success. Buffon felt that "one more defect and they could not have existed." This arthropomorphism was quashed by Beebe (1926) who suggested that a sloth in Paris would survive longer than Buffon in a tropical forest hanging by his limbs. Subsequent authors have also taken a more positive view in appraising the sloth's morphology. Ecologically speaking, the main point is the vast trophic opportunity available to any herbivore able to harvest energy from the photosynthetic surface of a forest. Except through secondary sources as fruits, seeds, saplings, or bark, this energy is untapped in any systematic way by other New World vertebrate herbivores.

It is quite probable that *Nothotherium* enjoyed a similar adaptive advantage, browsing on desert vegetation such as creosote bush, yucca, and cactus that many of its mammalian competitors rejected.

Living Pilosa

Flower and Lydekker (1891) pointed out that the extinct ground sloths were morphologically intermediate to the two surviving families of Pilosa. They combined the head and dentition of the tree sloths (*Bradypodidae*) with the vertebral structure, limbs, and gait of the giant anteater (*Myrmecophaga*). Although it will climb under duress (Krieg, 1939), *Myrmecophaga* is more terrestrial than other anteaters. It is about two-thirds the total length of *Nothrotherium*, and weighs up to 43 kg. Presumably those characteristics shared by both anteaters and tree sloths are highly likely to have typified *Nothrotherium* and other ground sloths.

Living Pilosa have certain traits unusual among mammals, such as a relatively low body temperature, a low basal metabolism, and limited thermal regulation. Tree sloths and the arboreal anteater (*Cyclopes*) are remarkable in their tendency toward poikilothermism. The extreme hypoactivity, also typical of tree sloths and *Cyclopes*, is not characteristic of *Myrmecophaga*. Nevertheless the giant anteater is not inclined to escape enemies by flight (Krieg, 1944).

Despite its tropical habitat, the three-toed sloth (*Bradypus*) is quite vulnerable to hyperthermy and will succumb in captivity if no shade is provided (Britton, 1941). Under direct sun at 35°-40°C the rectal temperature of an individual observed by Britton (1941) rose to 40°C and the animal expired after about two hours. The two-toed sloth (*Choloepus*) ranges up to 8000 feet where it withstands the penetrating damp cold of the montane fog forests (Britton, 1941). In Chiriqui Province, where water freezes in the dry season, Enders (1940) reported two-toed sloths between 6000 and 7000 feet. "Adult sloths inhabiting these areas were found to differ from those taken at sea level, chiefly in the length and quality of the hair . . . very much like dressed beaver, both in texture and quality" (Enders, p. 5). It would seem that assumptions about sloths being climatically restricted to the warm tropics must be abandoned.

Living Pilosa are relatively independent of water. Britton (1941, p. 202) comments: ". . . sloths would not need to eliminate heat rapidly by sweating under normal conditions in their tropical forest environment." He found that captive sloths will take water regularly, lapping with the tongue like a dog. This is not a necessity in nature; Krieg (1939) claimed they never drink and that sufficient water is absorbed from their forage to provide a water balance. The feces are relatively dry, an observation that may help explain the unleached nature of Rampart Cave dung. Beebe (1926) mentions the large bladder of *Bradypus* and claimed he never saw one drink: ". . . it is probable that it obtains sufficient moisture in the tissues of the leaves."

Less is known regarding water consumption in *Myrmecophaga*, an animal inhabiting tropical savannas and presumably exposed to greater thermal stress than the tree sloths. Honigmann (1935) was unable to confirm Schomburgk's claim that this animal sweats profusely. Krieg (1944) reported that in the Matto Grosso the giant anteater licks dew from plants and may occasionally drink.

TABLE 2
Diet of the Ground Sloth, *Nothrotherium shastense*

Location and source:		Aden Crater, New Mexico Eames, 1930	Gypsum Cave, Nevada Laudermilk and Munz, 1934	Rampart Cave, Arizona Laudermilk and Munz, 1938	Present study
1.	Polypodiaceae	d			d
2.	<i>Adiantum</i> <i>capillus-veneris</i>			a	
3.	* <i>Pinus</i>				d
4.	* <i>Juniperus utahensis</i>		a		c (gen.)
5.	<i>Ephedra nevadensis</i>		a	a	c (gen.)
6.	<i>Typha</i>		d		
7.	Gramineae		a		c
8.	<i>Aristida</i>			a	
9.	<i>Phragmites communis</i>			a	
10.	Cyperaceae				d
11.	<i>Yucca brevifolia</i>		a,b (genus)		
12.	<i>Y. baccata</i>		a		
13.	<i>Y. mohavensis</i>		a	a (Mauv)	
14.	<i>Nolina</i>			a	
15.	* <i>Agave utahensis</i>		a		
16.	<i>Populus</i>			a	
17.	* <i>Juglans</i>				d
18.	* <i>Betula</i>				d
19.	* <i>Quercus</i>				d
20.	Chenopodiaceae	a			d
21.	<i>Atriplex</i>	a	a	a	
22.	Nyctaginaceae				b
23.	Cruciferae	a			
24.	* <i>Ribes</i>				b
25.	<i>Prunus</i>			a	
26.	<i>Cassia</i>			a	
27.	<i>Larrea tridentata</i>		a,b	a	b
28.	Malvaceae		b		b
29.	<i>Sphaeralcea</i>	a	a	a	
30.	<i>Sida</i>	?			
31.	<i>Petalonyx</i>		a		
32.	<i>Opuntia</i>			a	
33.	Onagraceae		b		b
34.	<i>Oenothera</i>		a		
35.	<i>Fraxinus</i>			a	
36.	Polemoniaceae				b
37.	<i>Physalis</i>			a	
38.	*Caprifoliaceae				b
39.	Compositae	a	a,b		b,c
40.	<i>Gutierrezia</i>	a			
41.	<i>Chrysothamnus</i>		a		
42.	* <i>Artemisia</i>				c
Major portion of diet:		dicotyledonous angiosperms	<i>Yucca</i> , <i>Agave</i>	<i>Ephedra</i>	
Upper Sonoran elements (*)		0%	24%	0%	42%

a=plant parts identified in dung

b=zoögamous pollen

c=anemogamous pollen, abundant

d=anemogamous pollen or spores, not abundant

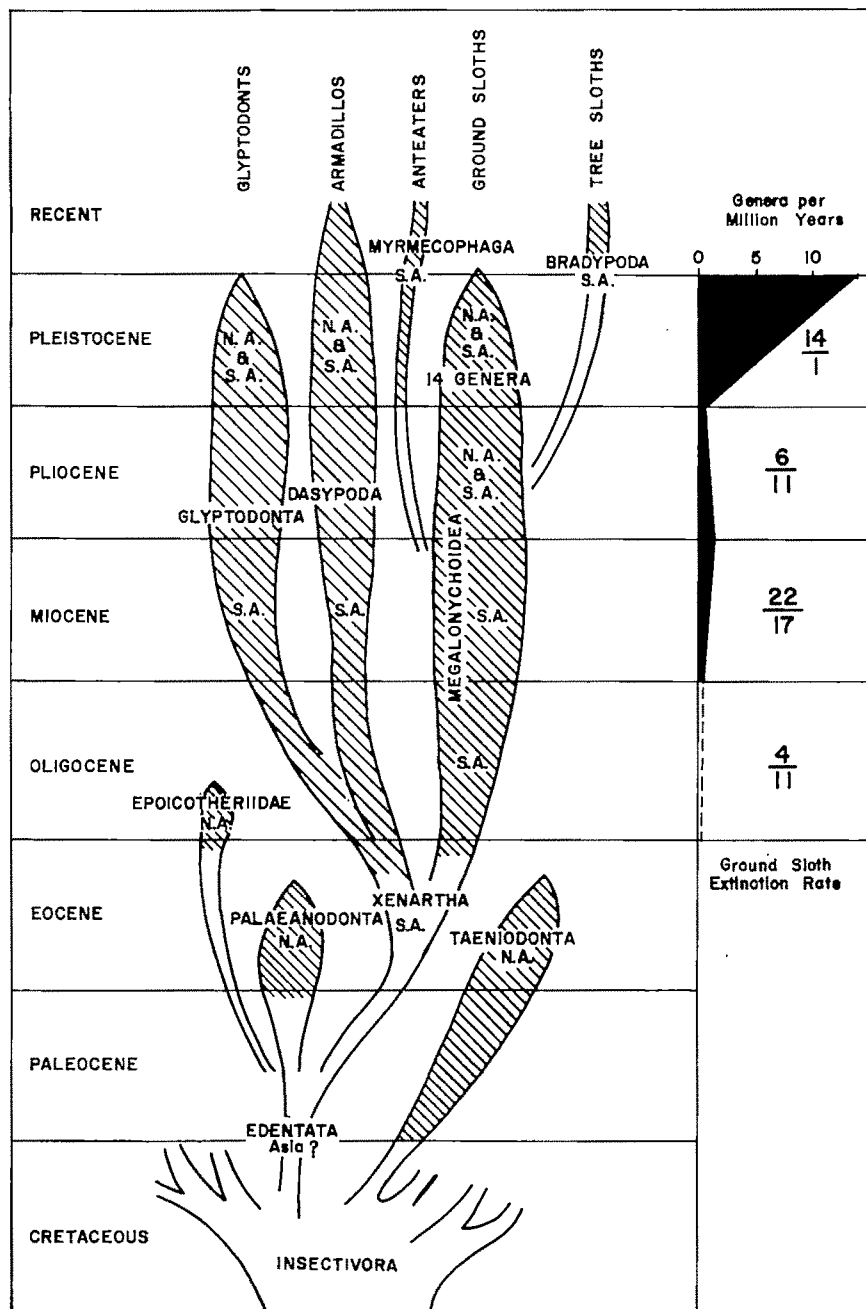


Fig. 8. Phylogeny of the Xenarthra. Ground sloth (*Megalonychoidea*) extinction rates shown for various periods of the Tertiary (adapted from Simpson, 1931 and 1945).

A generalized scheme for xenarthran evolution, adapted with little change from Simpson (1931), is shown in figure 8. Rates of extinction are plotted by dividing the number of genera last recorded in various geological epochs by the elapsed time for each. Unless the early fossil record of this group is found to be vastly richer than presently known (for example, 170 instead of 24 generic extinctions in the Miocene), there is only one epoch of strikingly high extinction rate, the Pleistocene. The group did not decline gradually in the Late Cenozoic or (although this is not shown in fig. 8) in the Early Pleistocene. In the Late Pleistocene it disappeared suddenly.

Paleoecology of Nothrotherium

All ground sloths were herbivores, as are living tree sloths. In view of their peculiar dentition it would seem improbable that they could have grazed extensively. Nevertheless, Eames (in Lull, 1930) found leaves, stems, and inflorescences of grasses and sedges in the dung of *Mylodon*, an assemblage quite different from that Eames encountered in dung of New Mexican *Nothrotherium*. Salmi (1955) found mainly herb pollen in *Mylodon* excrement.

Unlike *Mylodon*, *Nothrotherium* was a browser. Individuals at Gypsum Cave had fed on yucca (Laudermilk and Munz, 1934). Those at Rampart and Muav Caves had devoured cholla cactus, creosote, saltbush, and various herbs; *Ephedra* stems filled much of the dung balls (for complete list see table 2). Crystals of calcium oxalate, a secondary plant substance typical of Cactaceae and certain other plants, constituted over 50% of the fine-sieved fraction of dung from Gypsum Cave. In New Mexican coprolite Eames (1930) found abundant dicotyledonous twigs, especially of the mallow *Sphaeralcea*.

A capacity for browsing extensively on the desert shrubs consumed by *Nothrotherium* is not shared by existing large mammals, native or introduced. *Larrea* is shunned; *Gutierrezia* and *Chrysothamnus* poison domestic livestock; yucca fibers may cause compaction; oxalate crystals cause hemorrhage in sheep. Apparently these plants were among the normal diet of ground sloths. Thus the extinction of *Nothrotherium* must be considered ecological loss without replacement, an anomalous event that is rare but not unknown in the fossil record (e.g. mosasaurs in the Cretaceous).

Before dung studies had appeared, the gross morphology of *Nothrotherium shastense* led a foremost specialist of the group to consider it "... an animal living almost habitually in the dense jungles and forests or in regions having a heavy stand of timber" (Stock, 1925, p. 34). It is sobering to find that skeletal features are not completely reliable in framing deductions about habitat. On the other hand, Stock was correct in surmising that certain species of *Nothrotherium* must have inhabited mesic forests or savannas. The record of the genus in Brazilian caves obliges us to include the moist tropics within its domain. Probably it evolved from the moist tropics into the arid Southwest.

Other features of life history are not revealed by the fossil record. Clues to behavior and physiology of the extinct sloths may be found among their living relatives.

and *Nothrotherium* in the Southwest. The association of ground sloths and ceramics in the West Indies (Harrington, 1921; Aguayo, 1950) evidences survival there into late postglacial time. A similar claim for Sandia Cave, New Mexico (Hibben, 1941) has not been supported by findings elsewhere in the Southwest.

At present the stratigraphic record indicates that most, perhaps all, Pleistocene ground sloths flourished throughout the period of climatic changes, surviving four glacial and three interglacial intervals. They disappeared during the early postglacial period. West Indian sloths may have been the last survivors. On this basis it seems impossible to attribute ground sloth extinction to climatic change.

The Fossil Record

In the Pleistocene fourteen genera of ground sloths ranged from Alaska (Stock, 1942), and Northwest Territories (Stock and Richards, 1949) throughout North America, the Greater Antilles, Central and South America to Ultima Esperanza. Like the other Xenarthra, the Pilosa underwent their initial evolution in South America. They appear in North American deposits by the late Miocene or early Pliocene (Simpson, 1945). Among the native South American Tertiary mammals (liptoteria, notoungulates, old native rodents, marsupial carnivores, etc.), only the edentates invaded North America extensively.

Invasion of South America by Holarctic herbivores (perissodactyls, artiodactyls, lagomorphs, proboscideans) and their predators (modern carnivores) is generally held accountable for extinction of various native mammals (Simpson, 1950). Such an inference will not readily explain edentate extinction.

All sloths possess a peculiar dentition lacking enamel, an inturned foot structure insuring slow gait, and many primitive anatomical characteristics usually lost in advanced members of other orders. Their odd morphology has not inspired confidence in their evolutionary potential. "It would seem impossible that they could have survived and evolved in any reasonably competitive atmosphere or environment" (Gazin, 1956, p. 341). Nevertheless the fossil record reveals that ground sloths did just this. Throughout the late Cenozoic in both hemispheres they coexisted with a highly varied modern ungulate fauna.

Among the large New World herbivores the Pilosa are unique in reaching the West Indies. This feat may be explained in terms of the well-known swimming ability of tree sloths. Invasion across water barriers of both continental North America and the West Indies constitutes further evidence of their adaptability.

Ecologically, the ground sloths were euryoecic, occupying the Sonoran and Mojave Deserts (*Nothrotherium*), the temperate mesophytic forests of eastern and western North America (*Paramylodon*, *Megalonyx*), the subarctic taiga of Alaska and northern Canada (*Megalonyx*), the cool steppe of southern Patagonia (*Myiodon*, *Glossotherium*), as well as various tropical savannas and forests which are often assumed to have been their preferred habitat.

Possibly here, and elsewhere in the profile, manganese is a more sensitive indicator of climatic change than is pollen composition.

Our present climatic sequence may help to resolve a discrepancy in climatic history as interpreted by Wilson (1942) and Laudermilk and Munz (1938). From their studies of plant remains the latter concluded that "... when the ground sloths inhabited Rampart and Muav Caves, the flora and presumably the climate were essentially the same as those of the region today" (p. 278). This agrees with the pollen analysis of superficial layers, which we assume were the source of dung studied by Laudermilk and Munz.

Wilson (1942) commented on the presence of mammals (*Marmota*, *Oreamnos*) thought to be of boreo-montane distribution. Most of these specimens came from deeper levels of the cave, and thus would fall mainly into pollen zone (b), a period of cooler or wetter conditions. Undated evidence of a past cooler, wetter climate can also be adduced from the quantities of travertine left by former springs and seeps in the vicinity.

Wilson reported a cranium of the Lower Sonoran lizard, the chuckwalla (*Sauromalus*) at a depth of five feet. This is in accord with our evidence of a warm-dry climate during the initial phase of cave filling.

Attempts at more critical comparison between megafossil, microfossil, and biogeochemical evidence must await future excavation. At present we can identify a threefold climatic sequence in the fossil record of Rampart Cave: warm-dry, cool-moist, warm-dry.

EXTINCTION OF GROUND SLOTHS

The cause of disappearance dominates speculation about *Nothrotherium* and other gravigrades. How can this phenomenon be explained?

In studies of *Myiodon* dung from Patagonia, Auer (1954) and, especially, Salmi (1955) adopted biogeochemical and palynological methods in an effort to resolve the problem. Apparent copper and cobalt deficiency led Salmi (p. 332) to conclude that "... the resulting deficiency diseases in all probability had a decisive effect later by leading to their complete extinction in all parts of the globe."

Although we have been unable to sustain Salmi's interesting hypothesis, we acknowledge that his pioneering and provocative paper inspired our present studies of sloth dung. Before evaluating our findings with regard to copper and cobalt we will attempt a general scrutiny of the extinction record as it applies to ground sloths. The phenomenon involves basic questions of Pleistocene biogeography (Martin, 1958). Extinction of the Pleistocene megafauna is a chronological event widely used in stratigraphy, and the problem is of practical as well as theoretical importance. Particularly significant are the terminal dates of survival, the rates of gravigrade extinction, the ecology of *Nothrotherium* as deduced from its feeding habits, and the ecology of the living Pilosa, the tree sloths and anteaters.

Chronology

Radiocarbon dates of sloth dung from surface layers in *Myiodon*, Palli Aike, Gypsum, and Rampart Caves are remarkably concordant (table 1). They provide a terminal survival date of about 8500 B.P. for both *Myiodon* in Chile

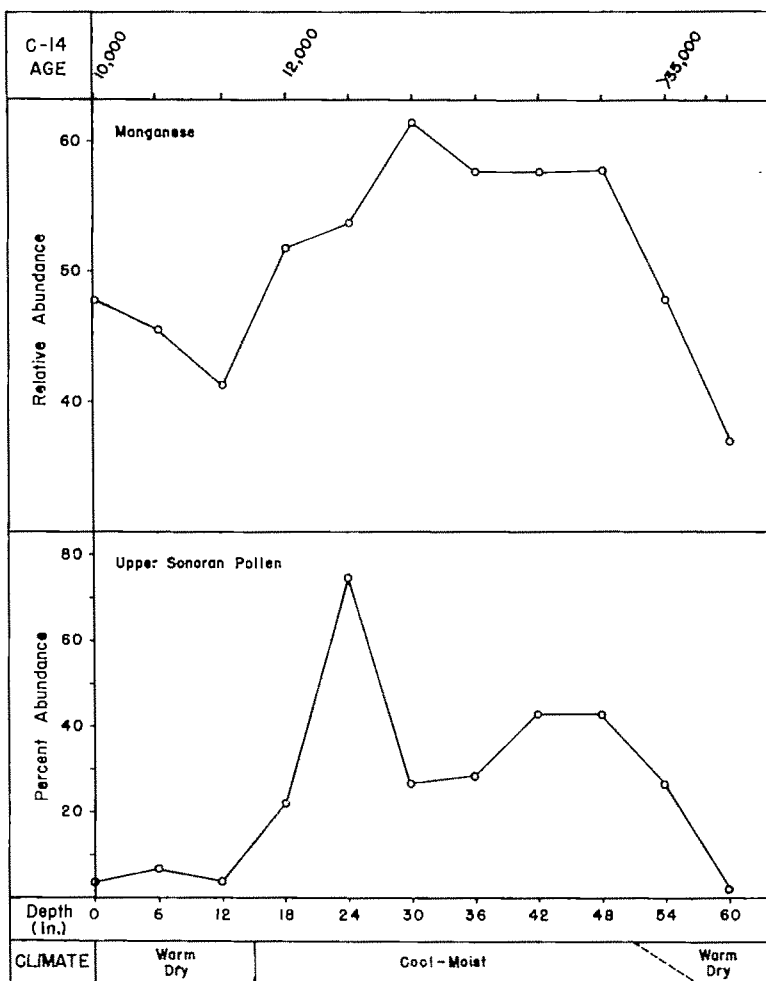


Fig. 7. Abundance of manganese (upper curve) and of Upper Sonoran pollen (lower curve). In each case high values reflect relatively cooler and/or wetter climates; low values reflect drier and/or warmer climates. Radiocarbon age in years before present at the top. The manganese curve was obtained by emission spectrography (see text). For absolute manganese values see footnote in trace element chapter, added in proof. The percent abundance of Upper Sonoran taxa is the sum of *Artemisi*, *Ribes*, *Caprifoliaceae*, *Juniperus*, *Pinus*, *Betula*, and *Gramineae*.

of variation. In general the two curves follow each other. Warm-dry conditions occurred at levels 60, 54, 12, 6, and 0; cool-moist conditions occurred from level 48 through 18.

Both curves indicate an arid maximum at level 12; this may represent the Alleröd interval. The manganese curve suggests a slight climatic reversal above level 12, as might be expected if the effect of Upper Dryas-Valders age cooling was felt in the Southwest. Support for such a change is not evident in either the pollen record or in Lauder milk and Munz' study of surface dung.

The next step is animal ingestion. Fortunately, manganese is hardly affected by metabolic processes (Underwood, 1956) and resists digestive absorption. The last link between the past climate and the present study is the dry dung deposit in Rampart Cave.

In this fashion we propose to distinguish relatively humid and relatively arid periods. This hypothesis was tested by comparison with the behavior of other elements and by comparison with the change in climatic indicators encountered in pollen analysis.¹

CLIMATIC CHANGE

Despite uncertainties in means of pollen dispersal and the formidable internal variation in our pollen diagram, it is possible to recognize three pollen zones: (a) a warm-dry interval from the surface to level 12; (b) a cool-moist interval from level 18 to 54; (c) a warm-dry time represented by level 60 and in certain subsamples of level 54. Zones (a) and (c) may have been equivalent in climate; they share a common feature, dominance of zoögamous Compositae. Subsample 4 of level 54 is dominated by pollen of the desert shrub *Larrea*, also present in lower frequency in levels 6 (0.4%), 12 (16.4%), and 18 (0.4%).

During the period represented by zone (b) there was sufficient ecological displacement to bring a juniper-sagebrush savanna, locally with birch, down to 1700 feet. In terms of life zones this represents an Upper Sonoran environment roughly 2000 to 4000 feet below its present lower altitudinal limit in the Grand Canyon.

A semiquantitative comparison of climate as recorded by manganese abundance and pollen composition is shown in figure 7. On grounds of its solubility characteristics, explained above, the manganese ion was selected as the most promising biogeochemical indicator of climatic change. Admittedly, both pollen and manganese curves incorporate certain uncontrollable sources

¹ Recent quantitative determinations by Sabels at the spectrographic laboratory of the Department of Geology, University of California at Los Angeles, refine our qualitative data presented above. The following results were obtained on manganese, copper, and cobalt.

With palladium and germanium as internal standards for manganese and copper (Vanselow and Liebig, U. C. Berkeley, 1945), an artificial plant-feces base powder was prepared. Using the intensity ratios Mn 2576/Pd 3461 and Cu 3247,3274/Ge 2754 it was found that the abundance of manganese (in Rampart Cave material) varied between 200 and 1000 ppm. Samples from levels 18, 54, and 60 contained 200 to 300 ppm, those from levels 0, 6, 12, 36, 42, and 48 contained 500 to 700 ppm, those from levels 24 and 30 contained 800 to 1000 ppm manganese.

Copper in excess of 100 ppm was found in samples of the 6-, 12-, 24-, 54-, and 60-inch levels. The copper content of samples 0, 18, 30, and 48 varied between 15 and 40 ppm.

No cobalt was detected in samples 0, 6, 24, and 30. Faint traces (order of magnitude of one ppm) were found in the 12-, 18-, and 36-inch samples, and measurable traces (order of magnitude of 10 ppm) were seen in the 42- through 60-inch samples. Thus if *Nothrotherium* extinction were to be explained in terms of cobalt deficiency, as measured in the feces, it should have occurred earlier than 12,000 B.P. in the time interval represented by the 30-inch dung strata.

The suitability of manganese abundance studies for paleoclimatic interpretations of cave strata was borne out by more quantitative work on dry and wet caves. Thus the spectrographer can guide tedious pollen studies and costly carbon dating by rapid surveys of cave profiles. This approach is presently being employed by the three authors.

oxides like pyrolusite, MnO_2 (fig. 6). In an arid climate we assume that the environment of the lower Grand Canyon was alkaline, with pH above 7. No, or very little, soluble manganese would be expected. Under humid conditions, slight acidity of the environment and reducing factors (decaying plants) will provide greater abundance of divalent manganese ions. Transitions between arid and humid climates seem to coincide with transitions between insoluble and highly soluble manganese compounds in the stability diagram (fig. 6). This mechanism, if effective, will supply sufficient manganese to plants living under humid and semihumid conditions but will cause shortage in plants of arid to semiarid environments.

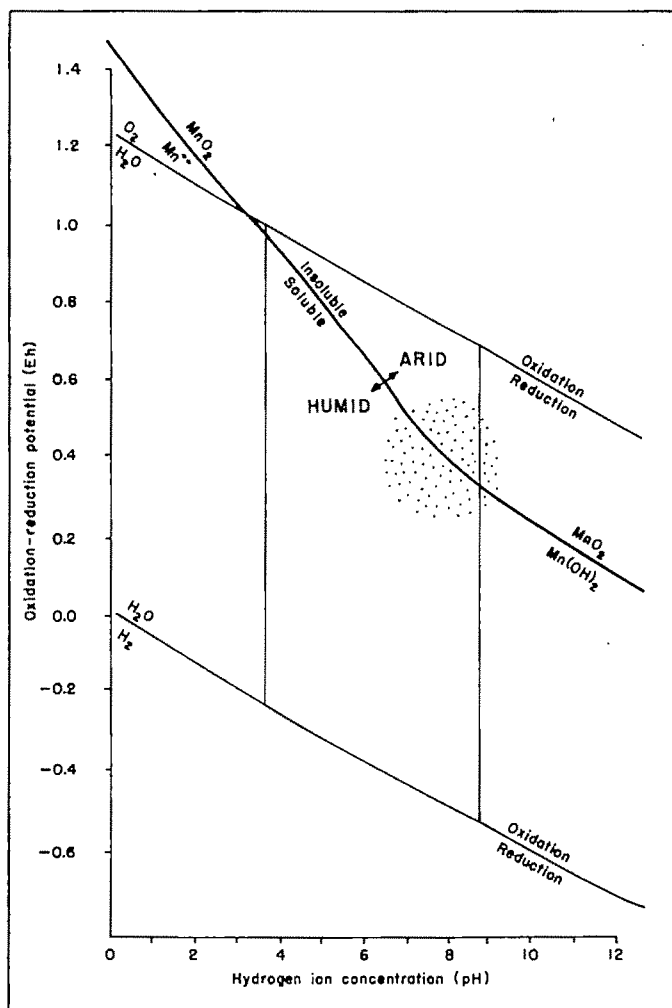


Fig. 6. Stability field of manganese compounds, modified after Krauskopf. Rampart Cave environments fall into the shaded circle.

Ti, V, Fe, Ni, Sn, Co, Zn, Ag, P, and Cr, the first three seemed to be of greatest significance as climatic indicators under the conditions at Rampart Cave.

The results of the emission spectrographic study appear in figures 5 and 7. The data were reproduced in three successive runs. A discussion of certain elements and their climatic or metabolic interpretation is given below.

Copper.—Copper was present in all samples. If 1.0 is taken as the density of absolute darkness, the density of the Cu lines varies between 0.28 and 0.50. There was no obvious trend relating time and abundance of copper. Considering that a marked intensification of the observed lines 3248 Å and 3374 Å must take into account matrix effects (Webb and Fearon, 1937), the absolute abundance is estimated to have been in order of magnitude of 100 parts per million at any time. Presumably *Nothrotherium* did not suffer Cu deficiency.

Cobalt.—The sensitivity limit of the instrument for Co lies in the order of magnitude of 10 parts per million. In no sample examined did the abundance of cobalt exceed this limit, so that no further statement concerning its abundance can be made. The range critical for deficiency diseases for ruminants lies between 1 and 10 parts per million in the food material (Underwood, 1956). As the sensitivity of the instrument used by Salmi is 1 part per million (1955, p. 318), and metabolic extraction of 10 to 90% of the food cobalt is quite reasonable (see discussion below), one is unable to establish whether or not *Myiodon* in South America or *Nothrotherium* in Arizona were eliminating minute amounts of cobalt. More sensitive techniques must be applied to decide this question.

Sodium and potassium.—Given arid conditions and a suitable topography, surface salts accumulate, forming alkali soils. The same compounds form from humid soil solutions, but they are removed in ground water and cannot accumulate. It follows that abundance of alkali in soils, plant tissue, and feces should be taken as an indication of prevalent dry (arid) climate. The bead effect can be used as a quick climatic indicator.

Manganese.—The chemical behavior of manganese depends upon two processes, which individually lead to opposite results. These processes consist of leaching of divalent manganese in solution, mainly as the bicarbonate, and precipitation of very insoluble hydroxides and oxides of trivalent or quadrivalent manganese. In contrast to other elements (V, Cr), the lowest state of oxidation (low Eh values) gives the most mobile ions, while higher oxidation states (high Eh values) are connected with a fixation of the element (fig. 6). What happens to the element will therefore depend on the access and amount of oxygen.

The pH of circulating waters is also of great importance in the geochemistry of manganese. Availability in general decreases with increasing pH. Manganese shortage seems to occur in two very different ranges of soil pH. The one range is in extremely acid soils, with pH less than 4 (Everglades, Florida), where nearly all the manganese has been removed by leaching of the manganous ions which have been made soluble by the acid conditions. The other range of manganese shortage is above pH 7. On such soils plant uptake is very low, although chemical analyses of soils show ample total manganese. The cause of the manganese shortage is its presence in very insoluble higher

ing habits. Urine excretion will simulate weathering. *Nothotherium* was probably an animal of high water economy. It may have existed largely on metabolic water, a conclusion based on studies of living sloths (see later discussion).

Processing of Samples

The composition varies from dust to coherent dung balls containing sizeable plant remnants. Therefore, great care must be taken in the preparation of representative samples.

They were processed as follows: a. quartering (homogenizing); b. pulverizing of the last fraction; c. combustion at 500°C. in a closed platinum crucible; d. pulverizing and quartering of the ash; e. mixing with spectrographic grade graphite powder, ratio 1:3; f. arc exposure until volatilization is complete.

Samples reacted differently when ignited in the platinum crucible. Some gave off ammonia and sulfur (see fig. 5). The sulfur condensed at the cooler parts of the crucible. When exposed without admixed graphite for one minute, at nine amperes current and 5 mm electrode distance, these samples did not arc to completion. Instead they left a glass bead residue. During this interval the excitation voltage remained low, 25 volts. Those samples which formed no bead and arced to completion were characterized, after a brief initial low-voltage interval, by an excitation voltage of 50. Variation in ionization potential of different chemical elements and their influence on arc temperature account for this effect. As a consequence, if there is an abundance of alkali metals present,

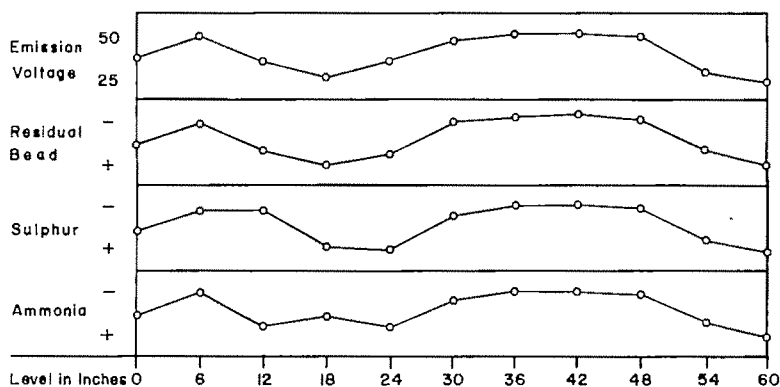


Fig. 5. Qualitative observations of sloth dung samples during spectrographic processing (see text).

the arc temperature stays low and most other elements fail to volatilize. In this case complete arcing requires admixture of graphite powder. Behavior of samples upon burning and arcing is shown in figure 5.

Results and Interpretation of Emission Spectrography

Semiquantitative interpretation of the abundance of elements by densitometry leads to a comparison of the relative abundance of every element in different samples. Among the elements Na, K, Mn, Cu, Mg, Ca, Sr, Al, Si, Pb,

tion of the slide from level 6. Although it is possible that a few *Ostrya* were included in the birch count, most grains showed an unmistakable *Betula* pore structure.

The small but appreciable percentages of birch, higher than one might expect as a result of wind transport alone, imply that birch trees grew near Rampart Cave in the Late Pleistocene. In Arizona Kearney and Peebles (1951) describe the present distribution of water birch (*Betula fontinalis*) as including the North Rim of the Grand Canyon between 7000 and 8000 feet, mostly along streams and often forming thickets. Little (1950) locates it within piñon-juniper woodland and ponderosa pine forest zones, 5000 to 8000 feet altitude. The fossil pollen record is a substantial indication of climatic change.

(d) *Cupressaceae, probably Juniperus*.—Pollen of the cypress family was present but very scarce in levels 18, 30, and 36. It dominated the original count and recount of level 54, but was absent in the sample reruns (subsamples 3 and 4). The assignment of all cypress-type pollen to the genus *Juniperus* can be defended in the absence of *Cupressus* from the Grand Canyon and the present distribution of juniper throughout the area at 3000 feet and above.

Several twigs and a seed found in the pack rat midden of the 36-inch level constitute rather sound evidence that juniper grew at the level of the cave, at least 1300 feet below their present lower limit.

Juniper pollen is shed in winter in southern Arizona, and its abundance in level 54 probably indicates winter residence of the sloth at that time.

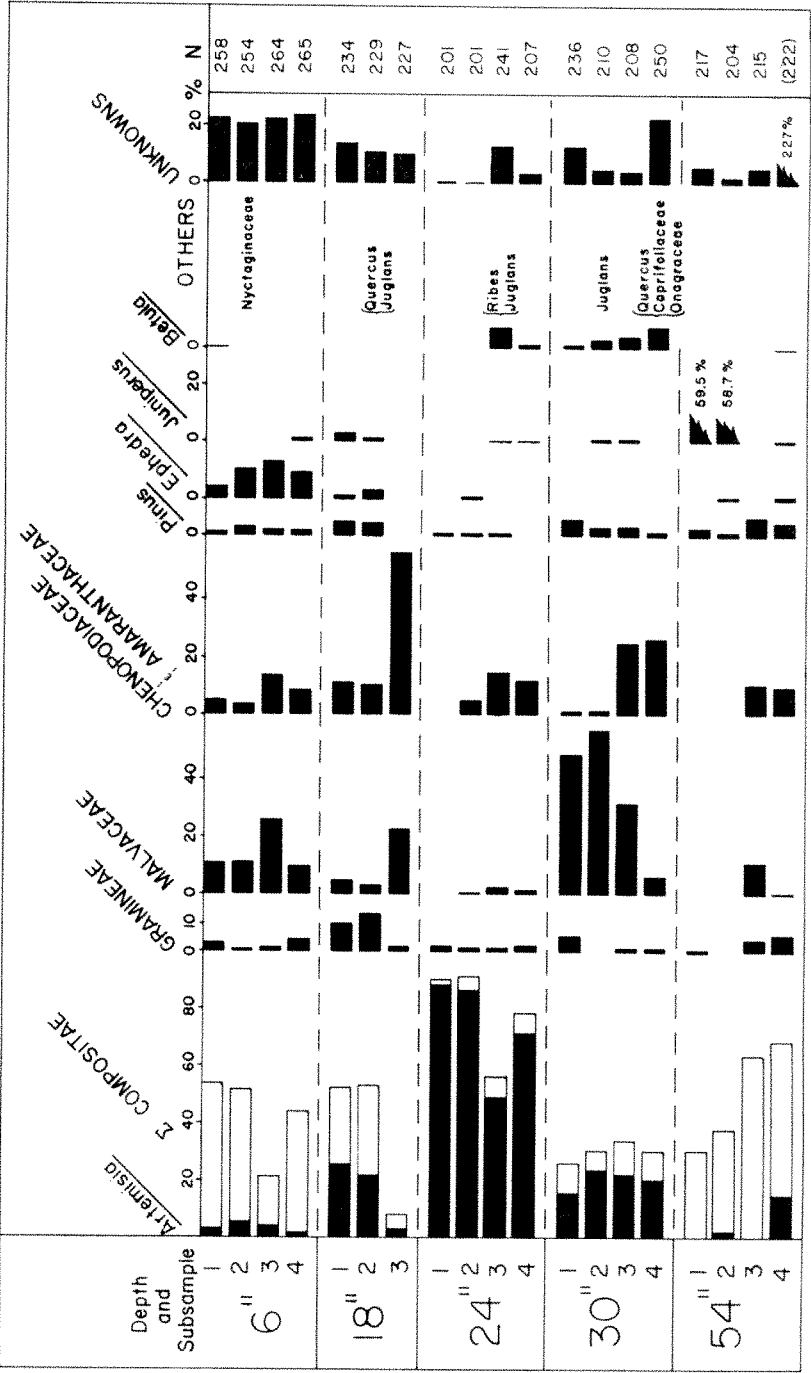
(e) *Rare occurrences*.—The following pollen types of possible climatic significance appeared rarely. None were seen in the original sample series used in constructing the pollen diagram: *Abies*, fir, level 30; *Alnus*, alder, level 54; *Ribes*, currant, level 24; *Symphoricarpos* or *Lonicera* (Caprifoliaceae), level 30; *Quercus*, oak, level 18; *Juglans*, walnut, levels 18 and 24.

All of these plants grow at elevations considerably above Rampart Cave, and presumably very little of their pollen wafts into Lower Granite Gorge at present. Although the possibility of accidental wind transport cannot be eliminated, it is notable that none of these rare indicators occurred outside of levels 18 through 54. In the case of zoögamous *Ribes* and *Lonicera-Symphoricarpos*, wind transportation is highly improbable, and it is more likely that the sloth included currants and honeysuckle in his diet. The lower altitudinal limit of *Ribes* in northern Arizona is 4000 feet (Kearney and Peebles, 1951).

In general the pollen record suggests a maximum vertical shift of 2000 to 4000 feet (600 to 1200 meters) in the vegetation gradient during the late Pleistocene. We attempted to seek additional evidence for this change in the biogeochemical nature of the dung.

TRACE ELEMENT ANALYSIS

A midden in the weathering zone is a geochemical anomaly undergoing dissipation. The same is true for dung deposits in wet caves. Dry caves unaffected by weathering preserve the original deposition pattern of trace elements in coprolite, regardless of the solubility of the mineral assemblages within the individual strata. The degree of preservation of the trace element pattern in dung will vary, depending on the nature of the animal's feces and its excret-



exceeds that to be expected by chance alone. It seems unnecessary to search farther than the feeding habits of the sloth for at least one obvious explanation. Unlike lake or marsh sediments, a fecal sample represents the integration of a fairly short period of flowering time, perhaps no more than a month. It should contain high percentages of whatever flowering plants were being ingested by the sloth and should vary drastically from season to season.

Unlike the zoögamous mallows and creosote, high percentages of anemogamous sagebrush and juniper do not necessarily reflect the dietary habit of the sloth. These plants produce pollen in sufficient quantity to dust all the vegetation in their vicinity, and the sloth might ingest their pollen in abundance without feeding on the plants themselves.

To learn more regarding internal variation, we analyzed replicate counts of five levels (fig. 3). The original count (subsample 1 in fig. 3) was made in July 1958 and used in constructing our pollen diagram.

In January 1959 a second count was made of residue from levels 6, 18, 24, 30, and 54. With the exception of a slight alteration in grass and *Ephedra* percentages, there was no difference between subsamples 1 and 2 which might not be attributed to chance.

The original sample bags of levels 6, 24, 30, and 54 were then removed from storage and a third and fourth subsample were extracted. In this case we failed to recover our original percentages (see subsample counts 3 and 4 in fig. 3). Applying the confidence interval tables for binomial distribution with n equal to 250 (Snedecor, 1956, p. 5), the probability that the difference between original and rerun samples is due to chance alone is less than 1% in each case. In level 54 the frequency of Cupressaceae dropped from 59% to zero.

To summarize, we find a high variation, both between levels and between dung subsamples within a single level. This can be explained most easily in terms of the seasonal progression in flowering of different plants eaten by the sloth. Admittedly the high subsample variation makes climatic interpretation of the pollen diagram less secure than one might wish. Only by considering all possible climatic indicators within the sequence is it possible to claim reasonable evidence of change.

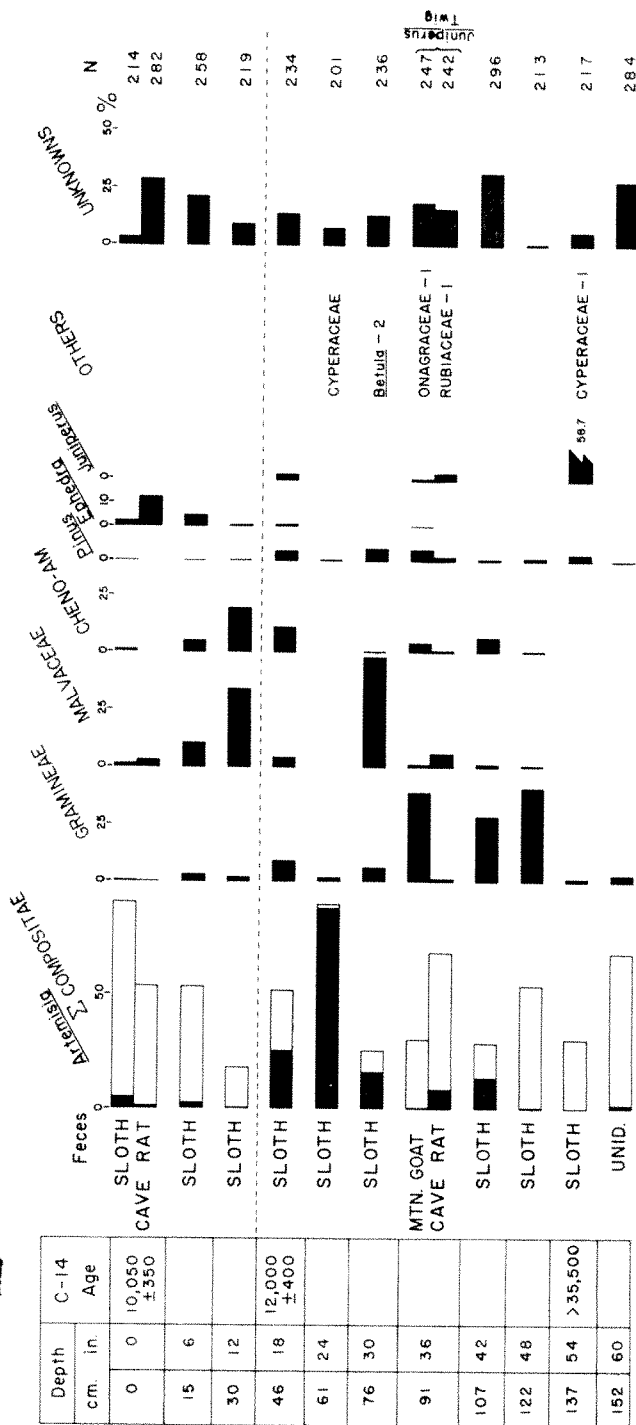
Climatic Indicators

At 1750 feet altitude Rampart Cave lies in the Lower Sonoran zone. Among 56 plants identified during their visit to the cave in June 1937, Lauder-milk and Munz listed the following shrubs: creosote, barrel cactus, catclaw acacia, ocotillo, burro weed, and incienso. Presumably these are the dominant feature of the landscape. Pollen of various plant taxa that do not occur at this elevation today appear in certain dung levels: a) sagebrush (*Artemisia*); b) pine (*Pinus*, mainly small pollen grains of the piñon type); c) birch (*Betula*); d) cypress-type (family Cupressaceae, probably *Juniperus*); e) rare occurrences of fir (*Abies*), alder (*Alnus*), walnut (*Juglans*), hornbeam (*Ostrya*), currant (*Ribes*), and honeysuckle (*Lonicera* or *Symphoricarpos*). We will discuss them in turn.

Fig. 2. Pollen profile of Rampart Cave. Cheno-Am = Chenopodiaceae plus Amaranthaceae. *Artemisia* (black bar) enclosed within sum of Compositae (open bar).



POLLEN ANALYSIS OF RAMPART CAVE



Radiocarbon dates of dung samples from the surface, 18-inch depth, and 54-inch depth are shown in table 1. The age obtained for level 18, 12,000 years, suggests an Older Dryas (Port Huron) correlation. The date of the surface sample, 10,000 years, is older than the minimum age of dung reported from adjacent Gypsum Cave in Nevada (8500 years). Perhaps *Nothrotherium* survived slightly longer at that locality.

The sample from the 54-inch level exceeded the sensitivity of Lamont Laboratory's gas counter and is at least 35,500 years old. The time span from surface to level 54 is thus at least 25,000 years and embraces the last glacial maximum of the Wisconsin age.

The radiocarbon dates can be used to estimate the average rate of fecal deposition. From the map in Laudermilk and Munz (1938), we estimate the area of the cave floor at 4875 square feet. If the top 18 inches of dung accumulated in 2000 years, the average annual rate would be 0.00075 feet, or 0.24 mm. Assuming an equal rate of deposition over the entire cave floor, this figure would require an average increment of about 3 2/3 cubic feet per year.

Deposition in the lower 36 inches was even slower. Since the 54-inch stratum is at least 35,000 years old, the average rate of deposition between levels 54 and 18 was at most 0.00013 feet (0.004 mm) per year, or an average annual volumetric increment of 0.6 cubic feet. The annual dung accumulation of a single animal must have exceeded this value greatly. Did the sloth occupy the cave only in the winter and move to higher altitudes to escape the summer heat? Low frequency of chenopod-amaranth pollen points to such a possibility. Was habitation erratic with several hundreds or even thousands of years intervening between periods of occupation? Or did sloths favor middens outside the cave and rarely eliminate within it? These details of sloth life history remain unknown; our main conclusion here is that dung accumulation within the cave was not continuous.

POLLEN ANALYSIS

Procedure and Theory

Organic material from each level was analyzed for pollen and spores. Hydrofluoric acid extraction served to remove the small amount of inorganic material present in the dung; screening, acetolysis, and heating in 5% KOH solution were employed to concentrate the plant microfossils. A few rodent and artiodactyl scats were analyzed separately (fig. 2). Amorphous organic material from the floor of the cave (level 60) could not be identified as to source. Abundant, well-preserved pollen was recovered, and a 200-grain count, exclusive of unknowns, was made at each level.

In three respects the final pollen profile differs from those of water-laid sediments. The frequency of unknowns is high (1 to 32%), zoögamous types are common, and there is great variation between adjacent strata.

An abundance of unknowns can be attributed to our unfamiliarity with zoögamous pollen types. The latter reflect the feeding habits of the sloth which ingested animal-pollinated flowers. Their pollen is not released in quantity into the atmosphere and is not abundant in most water-laid sediment.

The matter of internal variation between strata invited additional study. Except perhaps in the case of levels 0 and 6, variation between adjacent levels

to B. C. Arms for preparation of pollen samples, to C. Hedge for preparation of emission-spectrograph samples, to P. E. Damon, A. R. Kemmerer, E. B. Kurtz, and C. H. Lowe for comments on the manuscript, and to T. L. Smiley for encouragement and help at all times. The U. S. National Park Service generously supported Shutler's field work, and a National Science Foundation grant, NSF-G4803, facilitated Martin's pollen studies.

DESCRIPTION AND AGE OF THE DUNG

Eleven samples were collected in Rampart Cave at 6-inch intervals from the bottom to the top of a freshly cleaned face of an open trench. Except the deepest (60-inch level) all are dung samples, containing coarse plant fragments and fibers. Level 60 comprises a whitish powder containing black organic particles including pollen. It resembled the combustion products of levels 12, 18, and 24 and appears to be a product of slow natural decay of organic matter.

Three types of dung were recognized: (1) coarse, loose, light-colored plant fragments, often in lumps of two to three inches in diameter, which we assume represent the feces of *Nothrotherium*. Presumably these are fragments of dung masses; they match the description of Lauder milk and Munz (1938); (2) small, oval fecal pellets of a rodent, probably the cave rat, *Neotoma*; and (3) larger, lozenge-shaped dung balls of an herbivore, apparently an artiodactyl and possibly *Ovis* or *Oreamnos*, both found as fossils in the cave (Wilson, 1942).

Seven of the samples constitute sloth dung exclusively; cave rat scats were included in sloth dung from the surface and 30-inch levels. Level 36 is composed entirely of coarse plant material, cave rat and artiodactyl scats, seemingly the midden of a cave rat. Plant material in level 36 included three juniper twigs and a seed of juniper (*Juniperus*), spines of various shrubs and broken areoles of cacti, especially *Echinocactus* (determined by C. T. Mason and R. Hevly, University of Arizona Herbarium). It is possible that sloths did not inhabit the cave at this time. The maximum rate of fecal deposition, computed from the radiocarbon dates (see below), adds to the probability that sloth occupation in lower levels was not continuous.

TABLE 1
Radiocarbon dates from sloth caves

Locality	Laboratory number	Sloth Dung Yr. B. P.	Humic Acid Yr. B. P.	Stratum
1. Rampart Cave, Arizona	L-473A	10,050 $\pm$ 350	10,020 $\pm$ 350	Surface
2. "	L-473C	12,050 $\pm$ 400	11,950 $\pm$ 300	18"
3. "	L-473D	>35,500	>32,600	54"
4. Gypsum Cave, Nevada	C-222	8,527 $\pm$ 250		2' 6"
5. "	C-221	10,455 $\pm$ 340		6' 4"
6. Palli Aike Cave, Chile	C-485	8,639 $\pm$ 450		?
7. Mylodon Cave, Chile	C-484	10,832 $\pm$ 400		Layer C

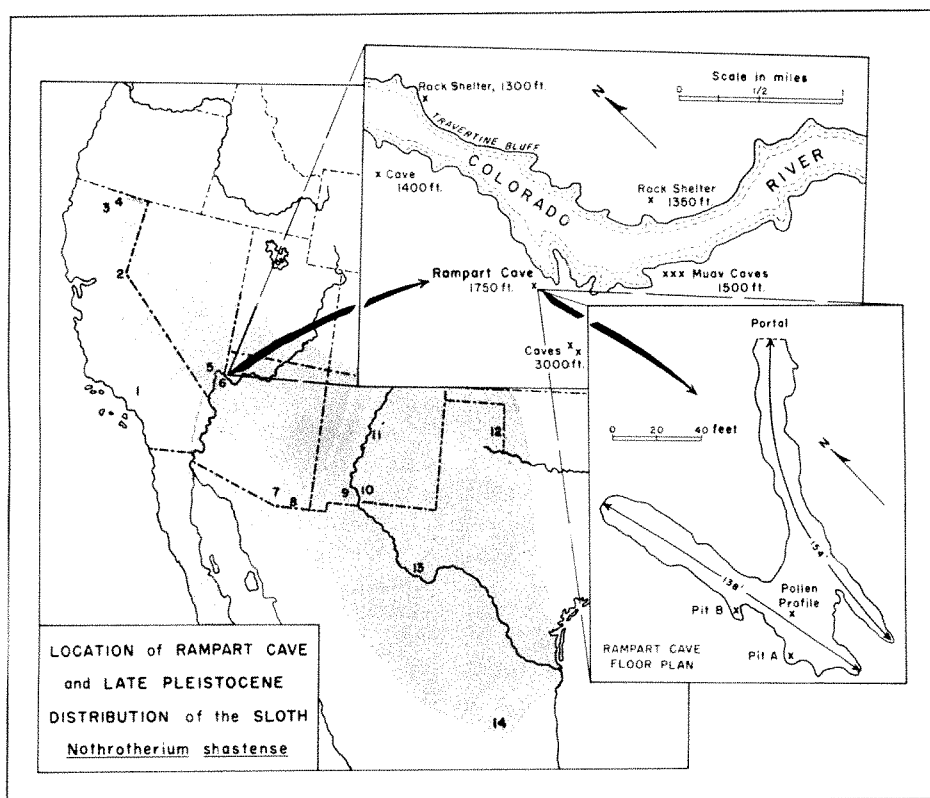


Fig. 1. Location of Rampart Cave and Late Pleistocene distribution of *Nothrotherium shastense*. Fossil remains have appeared at the following locations—California: 1. Rancho La Brea, 2. Hawver Cave, 3. Samwel Cave, 4. Potter Creek Cave, Nevada: 5. Gypsum Cave, Arizona: 6. Rampart and Muav Caves, 7. Ventana Cave, 8. Pyatt Cave, New Mexico: 9. Aden Crater, 10. Conkling Cave and Shelter Cave, 11. Sandia Cave, Texas: 12. Wheeler County, 13. Brewster County, Mexico, Nuevo León: 14. San Josecito Cave. Not shown is a record from Klamath County, Oregon.

Hibbard (personal communication) reports an Early Pleistocene record of *Nothrotherium* from below Pearlette Ash in Knox County, Texas.

Similar fossil remains of ground sloths, often including dung and certain soft parts, have been reported in caves in New Mexico (Lull, 1930), Nevada (Harrington, 1933), Tennessee (Mercer, 1897), and southern Patagonia, South America (summary in Rusconi, 1949). Through study of such deposits it may be possible to gain fresh insight concerning the ecology of gravi-grade sloths. As Salmi and others have realized, dung deposits may provide clues to the cause of sloth extinction.

ACKNOWLEDGMENTS

We are indebted to W. S. Broecker and E. A. Olson of the Lamont Geological Observatory for making available both the facilities of the Lamont Carbon-14 laboratory and their experience with this method. In addition we owe our thanks to Jane Gray for aiding in certain critical pollen identifications,

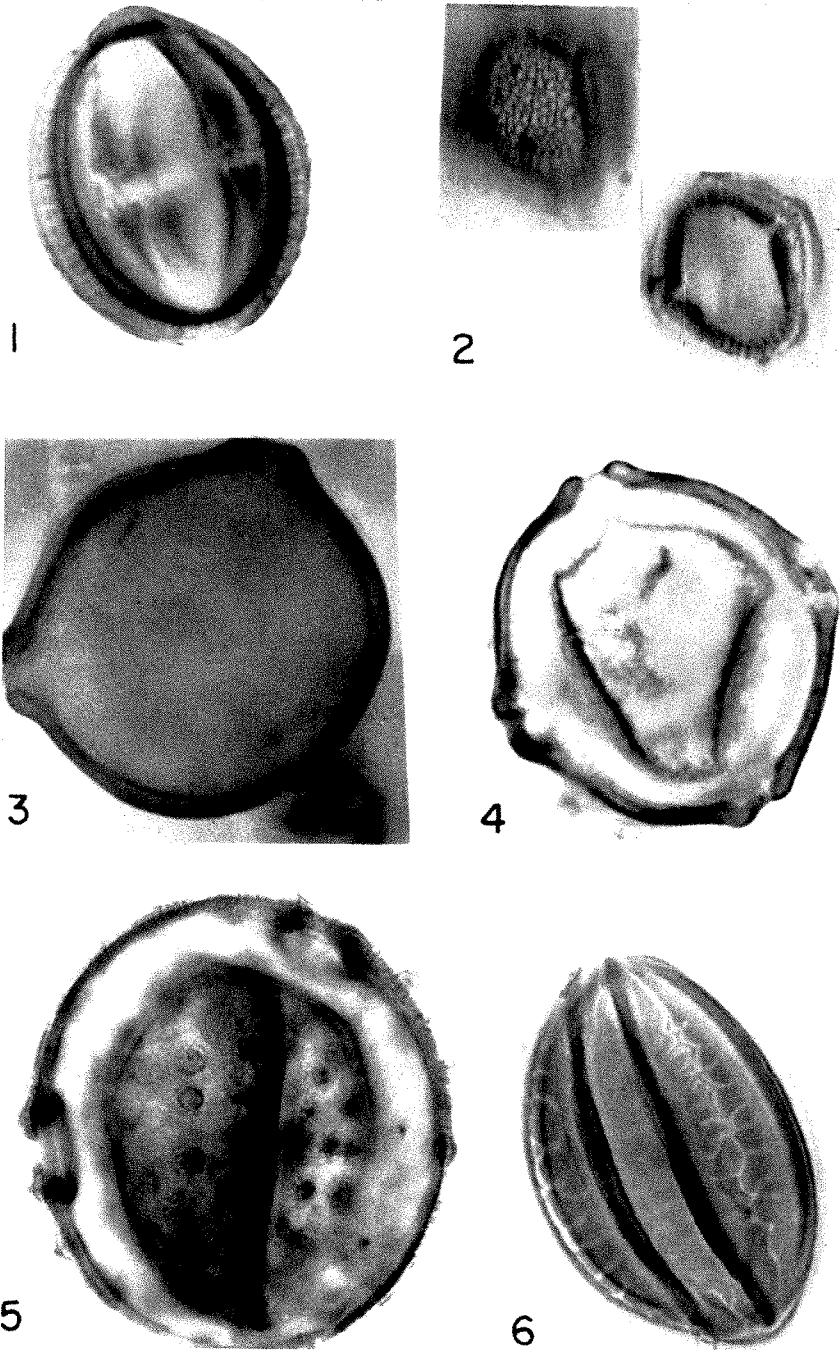


Fig. 4. Photomicrographs of pollen grains in sloth dung (not to scale): 1. *Artemisia*; 2. *Larrea* (1250x), high and mid focus; 3, 4. *Betula*; 5. Malvaceae, *Sphaeralcea* type; 6. *Ephedra, nevadensis* type.

(a) *Artemisia* (fig. 4).—Although sagebrush is wind pollinated, and may drift down into lower Granite Gorge at present, it is so abundant in certain levels that its past growth at 1750 feet seems certain. In level 24, 88 percent suggests that it was then browsed by the sloth as it is now by sheep. Identification to genus is reasonably secure; the long colpi, thick exine with columellae, and minute spines immediately distinguish *Artemisia* from *Franseria* and other anemophilous Compositae. Subgeneric identification was not attempted. There are 14 species in Arizona, ranging from 2500 to 9000 feet (Kearney and Peebles, 1951). In Arizona none of the shrubby artemisias are reported below 4000 feet. They are typical of cool desert, grassland, and woodland, including subalpine openings. Laudermilk and Munz reported only *Franseria* among the anemophilous Compositae seen near Rampart and Muav Caves.

(b) *Pinus*.—As shown in figure 2 pine pollen appears slightly more abundant in levels 18, 30, 36A, and 54. In the original 200-grain count the percentages varied from 0.1 to 5.8, a fluctuation that might be attributed to chance alone. To test this possibility pine frequency was recorded in a thousand-grain scan with the following results: level 0 (sloth)—1; level 0 (rat)—0; level 6—6; level 12—8; level 18—25; level 24—3; level 30—30; level 36 (mountain goat)—48; level 42—7; level 48—6; level 54—20; level 60—4. On this basis the increase in pine in levels 18, 30, and 36A cannot be attributed to sampling variation.

Admittedly this provides no more than a clue to the possible history of pine in the Grand Canyon. Frequencies of 5% pine pollen have been recovered in cattle tanks of the desert grassland in southern Arizona, roughly ten miles distant from the nearest isolated montane pine populations. Piñon-juniper woodland occurs near both north and south rims of Lower Granite Gorge, and Nichol (1952) maps isolated yellow pine stands within 40 miles of Rampart Cave. Small amounts of conifer pollen may be wind-transported into the area at present.

Conversely, piñon trees might have grown at the mouth of Rampart Cave and be entirely under-represented, if none of the dung samples were dropped during the season when the animals would have ingested pine pollen.

Taken by itself we would not draw climatic inference on the slight frequency change in pine pollen. Nevertheless there is a relationship between pine abundance and that of other cool climate indicators.

(c) *Betula* (fig. 4).—Two birch grains were observed in the first count of level 30 (subsample 1 of fig. 3). Six were observed in the recount (subsample 2) and eight in the sample rerun (subsample 3). Although none were noted in the original count of level 24, a total of 18 were found in the sample rerun (subsample 3) from that level. One was found outside the counted por-

Fig. 3. Subsample variation in pollen count of certain dung levels. The large numbers indicate depth of sample; small numbers represent individual replicate counts within that sample (see text). 227 percent "unknowns" in level 54 are mainly of *Larrea* (creosote bush).

RAMPART CAVE COPROLITE AND ECOLOGY OF THE SHASTA GROUND SLOTH*

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ABSTRACT. The shasta ground sloth *Nothrotherium shastense* inhabited Rampart Cave in the Grand Canyon of the Colorado River, Arizona for at least 25,000 years. During this interval occupation was probably discontinuous; radiocarbon dates of the dung from the surface of the cave are on the order of 10,000 years, from the 18-inch level 12,000 years, and from the 54-inch level older than 35,000 years. Dung samples collected at 6-inch intervals to a depth of 60 inches proved rich in well-preserved pollen. Within each level there is great variation in pollen content. In part this reflects seasonal change in flowering time of various plants growing adjacent to the cave. An increase in *Artemisia*, *Pinus*, *Betula*, Cupressaceae, and other montane trees and shrubs reveals that levels 18 through 48 represent a time of cooler or wetter climate with Upper Sonoran vegetation displaced downward 2000 to 4000 feet.

These samples were analyzed spectrographically for trace element content. On theoretical grounds the abundance of manganese proves a promising index of climatic change; when compared with the pollen evidence, there is a reasonably good fit between high manganese values and periods of greater moisture. These correspond to the Wisconsin glacial age.

Cobalt is very rare and copper is abundant in dung from all levels. There is no indication that a change in abundance of these triggered ground sloth extinction, as claimed by Salmi (1955).

Nothrotherium excelled as a browser in the arid Southwest. Some of its preferred food plants, as creosote bush, yucca, snakeweed, and cactus, are not harvested systematically by existing large desert herbivores. The ecological niche of *Nothrotherium* remains unfilled. Its extinction defies an obvious environmental explanation either in terms of trace element deficiency, competition, or climatic change. The cause of extinction must lie elsewhere.

INTRODUCTION

In 1936 a rich cave deposit of Late Pleistocene fossils and dung, notably of the ground sloth *Nothrotherium shastense* Sinclair, was discovered by a National Park Service employee, Willis Evans. The locality, named Rampart Cave, lies in the Lower Granite Gorge of the Grand Canyon, Arizona about four miles upstream from Pierce's Ferry (fig. 1). The cave opens near the base of the Muav limestone (Upper Cambrian) at an altitude of 1750 feet, approximately 4000 feet below the rim of the canyon and 750 feet above the Colorado River. Soon after discovery the U. S. National Park Service closed the cave mouth with a gate, preventing entry of unauthorized persons. Except for test pits and a trench, the fossil and dung deposit, five to six feet in depth, is preserved largely intact.

There are two important paleontological reports on Rampart Cave. Lauder milk and Munz (1938) identified plant material, including some pollen and spores, from the sloth dung. Wilson (1942) described a vertebrate fauna of at least ten genera in addition to the sloth. Our contribution concerns radiocarbon dating (Shutler at Lamont), pollen analysis (Martin), trace element studies (Sabels), and extinction theory. Our study is based on a 60-inch dung profile collected by Shutler in June of 1956. Exact location of the profile is shown on the cave floor plan (fig. 1).

* Contribution No. 14 of the Program in Geochronology.

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Mechanical disintegration may readily occur in such material and produce grain sizes comparable with predominate grain sizes in the sedimentary rocks.

The more indurated sedimentary and the crystalline rocks are also subject to mechanical disintegration, but it probably occurs at slower rates. The mineral composition of such indurated materials is thought to control the eventual particle size distribution.

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After quoting the original gross definition of gumbotil, Frye and others (1960, p. 185) state:

This definition is both empirical and genetic. As will be explained, it is this dualism of the definition that produces the present dilemma.

It is intimated that if gumbotil had been defined empirically and not genetically there would be no dilemma. If such features are to be defined without reference to origin, what will be done with the terms "till," "drift," "outwash," "valley train," "drumlin," "kame," "ground moraine," "delta," "alluvium," "colluvium," "sand dune," "beach," "stalactite," "volcanic ash," etc.? After all, what is the main use of classification and nomenclature if not to record historical conditions and events?

The authors cite eight clays in Illinois, Iowa and Kansas that have been called gumbotil (Frye and others, 1960, p. 187-189). Of these, two are said to be gumbotil, both empirically and genetically, and from the descriptions the present writer agrees. The other six are thought to be gumbotil empirically but not genetically, thus adding to the dilemma; then the authors proceed to point out ways in which the "samples" differ from gumbotil. This writer contends that these differences are definitive and that these clays should not have been called gumbotil. Some of these clays are calcareous, some are stratified, some contain no pebbles similar to those in underlying drift, none grades into unaltered till through zones of partly weathered till, and one is 30 feet thick. Furthermore, two of them are said to lie on Wisconsin till. Kay and his associates were quite familiar with tills of Wisconsin age and found no gumbotil on them. These till sheets are too young to have been weathered to gumbotil. In fact, the absence of gumbotil is one of several criteria for the separation of the Wisconsin from older till sheets. The authors are to be commended for having called attention to these misidentifications. As always, care should be taken to identify accurately before making interpretation.

Now what about the term "gley" that is proposed as a possible substitute for gumbotil (Frye and others, 1960)? But the terms "gley," "gleyed," "gleying" and "gleization" are not defined. Indeed, definitions of these terms are confused in English language literature.

The concept of the soil profile and the formation of gley as a part of this profile was started by Glinka in Russia and introduced in this country by Marbut (1927), as recorded by Leighton (1958, p. 704-706) and Frye and others (1960, p. 185). However, only three references to gley are found in the Marbut translation of Glinka (1927, p. 105, 168, 169). All refer to the normal profile as developed under certain climatic conditions. No reference is made to intensely weathered material such as gumbotil, and for a very good reason; the drifts of Russia are mostly of late Pleistocene age and too young to have been maturely weathered. Glinka never saw gumbotil and made no place for it in the Russian classification of soils.

The term "gley" is not listed in the Russian-English science dictionaries available to this writer. According to Russian language dictionaries and encyclopedias, translated for the writer by Miss Ada M. Stoffet of the State University of Iowa Library, the Russian word "gley" was derived from a Greek word that means glue or, as defined by Liddell and Scott (1925), "any glu-

tinuous substance, gum". As an adjective it means sticky, watery, muddy, marshy, gummy (Preobrazhensky, 1951). The Great Soviet Encyclopedia (1952) under "Glei (gley)" lists soil composed of anaerobic bacteria in marshy places and makes no mention of the soil profile.

It seems, therefore, that in Russia gley is any sticky clay, and of course all clays are more or less sticky when wet. A large variety of clays is included. No mention is made of genesis or parent material. Russian gley could be found in almost any area whether it had been glaciated or not. It is not a term that applies especially in Pleistocene geology.

Nor is gley mentioned frequently or clearly defined in standard works of soil science in the United States. Even Marbut (1951) did not use the term in ten lectures delivered in 1928. He had much to say about the soil profile as described originally in Russia, about laterite and lateritization, about soil classification and nomenclature, but did not even mention gley or gleying.

Even where the term "gley" does appear in American literature, its definitions and usages are little if any less general or more specific than in Russian. In the most recent edition of the Soil Survey Manual (1951) mention is made of

intensely gleyed layers as in hydromorphic soils (p. 175); G. (Horizon—developed wholly or partly by gleying. Involves saturation of the soil with water for long periods in the presence of organic matter. One may speak appropriately of a "gley soil" but hardly of a "gley horizon," since the genesis of the whole profile is involved. Besides the G., other horizons may be somewhat gleyed. Occasionally it may be necessary to differentiate in the description between fossil gley and active gley (p. 180); g: a gleyed horizon, as Bg or Bag (p. 181).

Any B zone has apparently been gleyed and is a gley.

The paragraph from page 184 of the 1951 Soil Survey Manual quoted by the authors (Frye and others, 1960, p. 186) seems to relate to "accretion-gley," but in this paragraph neither gley nor gleying is defined. That the gley of the Soil Survey Manual does not include gumbotil is suggested by the footnote (p. 152) which is as follows:

In the Middle West, the term *gumbotil* is applied to tenaceous clays, generally gray, plastic when wet, and hard when dry, which have been weathered from Nebraskan, Kansan, and Illinoian till during the interglacial period.

In the paper under discussion (Frye and others, 1960, p. 186), the quotation from Senstius (1958, p. 362) might have included the following: "The *underclay* of coal deposits is nothing else but fossil gley." This kind of gley called "peaty gley" seems unrelated to gumbotil.

Joffe lists six index references to "Glei" (1949, p. 56-57, 65, 418-432, 517, 601, 602). Mention is made of iron and calcareous concretions in loess ("pipestems" and "loess kindchen" of Pleistocene geology); glei or glei-like materials formed in fresh water or marine marshes; and clays due to gleying of glauconitic Tertiary formations in New Jersey. A close relation between podzols and glei-horizons is brought out, but the term "gley" is used in more than one sense and parent material is not important.

The four authors (Frye and others, 1960, p. 186) outline five ways in which gumbotil or gumbotil-like clays can be formed. Only one (5) results in

gumbotil as originally defined. Just how many and what of the genetic methods result in accretion-gley is not made clear. By numbers (2) and (3) accretion-gley is formed. The deposit resulting from number (1) would be calcareous, unless leached after deposition, stratified, and without pebbles; in fact these are the conditions that result in the formation of *varves*. If there are four or five or six conditions of formation and all are to be called gley, would not other modifiers besides "accretion-" be required? What would these other modifiers be? Especially, what kind of gley would gumbotil be if the term "gumbotil" were to be abandoned? If the four authors mean that there are only two genetic types of gleyed material, accretion-gley and material gleyed in situ, and the term "gumbotil" is abandoned, the type that is formed in situ is still left without a name. It should be noted that "Humic-Glei" and "Low-Humic Glei" soils (Thorp and Smith, 1949, p. 119), "Meadow soil or gley soil" (Robinson, 1949, p. 354) and "Gley Podzols" (Robinson, p. 361), "Peat-podzolic-glei soil" and "Peat-gley soil" (Joffe, 1949, p. 428), and "peaty gley" (Senstius, 1958, p. 362) are in current use pedologically.

In summary it should be said that the authors of this important paper should be commended for having brought this matter to the attention of Pleistocene geologists and pedologists; that gumbotil as originally defined can be distinguished readily enough from other clays; that ordinary care should be taken in distinguishing among clays of different sorts and origins; but that, in the opinion of this writer, gumbotil should continue to be called gumbotil, at least by Pleistocene geologists.

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REVIEWS

Historical Geology, 2nd ed.; by CARL O. DUNBAR. P. xi, 500; 406 figs., 20 plates. New York, 1960 (John Wiley and Sons, Inc., \$7.95).—A well planned and well executed book, full of interest and almost free from little errors.

Dunbar's treatment of historical geology is conventional. As with other texts written in English, the stratigraphy on which it is based is almost entirely that of the author's professional habitat, in this case the continent of North America. The development is systematically chronological, period by period, from early to late, yet with sufficient variety and intrinsic solidity to maintain interest.

The 1960 edition is the latest in a Yale-Wiley series that was begun by Charles Schuchert in 1915. Yet it is notably new. In particular, the number of illustrations has been increased by 59 over the first edition and the page size has been enlarged, making possible figures up to $7\frac{1}{2}$ by 10 inches. Larger size and improved clarity make the half-tones much more effective. Among the additions are several striking Zallinger reconstructions. Changes have transformed the chapters on "The Scale of Geologic Time" (radioactive chronometers), "Ice Sculptures the Final Scene" (new figures, radiocarbon, etc.), and "Mammals Inherit the Earth" (13 fine new illustrations).

Other methods of treatment are possible for historical geology. The stratigraphy of the whole world might be the basis for the geologic history. Structural evolution might be made the central theme. Description of the events of period after period might even be replaced by development of the principles of correlation and interpretation, with examples so chosen that in the end every period name would have meaning for the student. In spite of these and other possibilities, the old reliable type of text is likely to remain most widely used in America. Teachers may suggest course modifications, such as those proposed in the *Journal of Geological Education*, volume 7, pages 64-74 (1959), but when confronted by an actual alternative book may still choose Dunbar or something similar because local stratigraphy and history can be fitted so neatly into a course with such a text.

A. O. WOODFORD

The Mammals of North America; by E. RAYMOND HALL and KEITH R. KELSON. P. xxix, 1083 + 79 index. New York, 1959 (Ronald Press, 2 vols., \$35.00).—The large and carefully drawn maps showing the geographic distribution of every recognized species and subspecies of living or recently extinct North American mammal in these handsome volumes will be particularly useful to students of Pleistocene vertebrates as well as to systematic mammalogists. A brief introductory chapter outlines some major conclusions about the factors underlying the distribution patterns shown on the 500 maps and presents a theory of mammalian dispersal with numerous references to more detailed zoogeographic discussions. At the end of the work a chapter on collecting and preparing study specimens stresses the need for full and accurate field data. The extensive reference list is followed by full index, which is most conveniently printed at the end of each volume. End paper maps of life zones and political subdivisions are at once decorative and useful references.

Except for these brief general sections, the entire treatise is a systematic list of mammals. Keys are provided to species and higher taxa; these refer to both skeletal and external characteristics and are obviously designed for the professional student with adequate material at his disposal. Genera and species are briefly characterized, frequently in no more detail and sometimes less intelligibly than in the familiar small handbooks and pocket guides. Nearly all are illustrated, either by skull drawings or pen-and-ink sketches of the entire animal. Greater attention to details of tooth pattern would have enhanced the value of the illustrations of small skulls to paleontologists and others interested in using them for comparisons, but such features as are shown are portrayed accurately so the figures will materially aid students in identifying complete skulls. No other reference illustrates so many (538) different kinds of mammalian skulls. Type localities and marginal records are given to show the distribution of each taxon, together with references to the original description, descriptions of synonyms, and significant revisions of all recognized forms. No distinguishing characteristics other than geographic range are mentioned for subspecies, so that anyone working with marginal or dubious material would find it necessary to turn to other sources. Nor is anything said about the relationship between subspecies, and the absence of diagnoses prevents the reader from drawing inferences as to the course of phylogenetic development and speciation within polytypic groups. This seems a peculiar defect in a work of this magnitude. In view of the thorough bibliographic information provided in the Miller and Kellogg list (U. S. Natl. Mus. Bull. 205, 1955) the authors of the present volume could have made a far greater contribution by omitting some references and using the space for diagnoses and discussions of these matters. Technical names have been determined strictly on the basis of priority. This fundamental principle may be overworked, however, and actually lead to useless nomenclatorial confusion. To adopt *Dama*, the name by which the fallow deer of Europe has been known for over a century, for the White Tail and mule deer of North America, generally called *Odocoileus*, because of a reinterpretation of 18th century works, is carrying priority to the point of absurdity.

Grouping the Triconodonta with the Multituberculata in the Subclass Allotheria does not accurately represent the best current opinion on the relationships of these long-extinct Orders, but is scarcely pertinent to the subject of the treatise. More surprising is the grouping of the Canidae with the Feloid Carnivora and the statement that they have a divided bulla. Such defects are bound to creep into any work of this magnitude. They do not detract from its general value, but give an impression of hasty rather than careful compilation.

JOSEPH T. GREGORY

Miocene Floras of the Columbia Plateau; by RALPH W. CHANEY and DANIEL I. AXELROD. Quarto P. viii, 237; 44 plates, 32 tables, 1 map. 1959 (Carnegie Institution of Washington Publication 617 (Contributions to Paleontology), paper \$4.25, cloth \$4.75).—This paper is in two parts: Composition and Interpretation, by Chaney, and Systematic Considerations, by Chaney and Axelrod. It represents the results of many years of study of the Miocene

floras of central Oregon and will prove to be of value to all students of Tertiary paleobotany.

In Part II, Systematic Considerations, 69 species represented by megafossils are discussed, of which only 10 are new. This relatively small proportion indicates the scope of previous work on these and related floras. Much important clarification and correction of earlier confusion and mistakes is incorporated in this section. Three lists, *Nomina dubia*, Rejected species, and Systematic Revisions summarize this material in a convenient and accessible form.

Part I, Composition and Interpretation, by Chaney, discusses three large floras, the Mascall, Blue Mountains, and Stinking Water. Each is considered in detail under three major headings of Geologic Occurrence, Composition, and Paleoecology. These are treated with varying emphasis: in the discussion of the Mascall flora, for instance, the geologic occurrence occupies about 6 pages, whereas paleoecology takes up 28, not including the tables.

The lengthiness of the section indicates the detailed and exhaustive discussion of the factors of the ecology of the fossil floras. In accordance with the best methods of Tertiary paleobotany the fossils are considered always in the light of their living relatives. Each flora is divided into elements, based on the geographic distribution of the living types. Thus, the author recognizes the East American, East Asian, and West American elements in all three floras.

Elements, in turn, may be divided into components based on more detailed ecological factors. The East American element of the Mascall flora, for example, is divided into the Swamp Cypress component and the Appalachian component to correspond with the habitats of the living equivalents.

From detailed analysis of the requirements of these units, together with factors of numerical representation, the fossil floras are divided into associations. Consideration of the association augmented by analysis of the local representation of individual species and larger groups leads to conclusions concerning topography and climate at the time the fossil flora was laid down. Numerical representation of species is taken into account, the factors controlling it having been fully considered in the section on Composition. Throughout, the available evidence from microfossils, vertebrate remains, and others is considered insofar as it is available and pertinent.

This section concludes with a discussion of the relationships of the three floras with adjacent floras of middle Miocene age, in which similarities and differences are briefly considered, and a thoroughgoing analysis of the factors leading to determination of the age of the floras.

The geologic evidence, not entirely satisfactory, is added to by the evidence of the outside distribution and paleoecology. In this, particular emphasis is laid on the progressive change to cooler and dryer conditions during Middle and Late Tertiary time with concomitant gradual disappearance of swamp plants and appearance of dry-region plants.

The author's style is, as usual, an example of simple straightforward prose of clarity and conciseness, with occasional glimpses of relaxed good humor. In this reviewer the paper evoked nostalgia for the beautiful western mountains and deserts.

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THE SCANDINAVIAN CALEDONIDES A REVIEW

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On the occasion of the Geological Congress of 1960 arranged by the Nordic countries, descriptions of the geology of the Scandinavian Peninsula have been edited in English and have thus been made available to a wide circle of readers. The descriptions of the Caledonides, which like the other main geological units of the peninsula are divided between Norway and Sweden, have appeared separately in the parts falling within each of the two countries. Thus the present short digest of the geology of the Scandinavian Caledonides may be useful also as an introduction to the literature on the Norwegian and Swedish parts, which show some discrepancies, at least in the nomenclature.

The Caledonides form the western part of the Scandinavian Peninsula; the greater part on Norwegian territory. The eastern Caledonian margin is formed by a range of nappes overthrust upon autochthonous Cambro-Ordovician sediments, which in turn rest upon the peneplaned surface of the Precambrian rocks of the Baltic shield. Between $61^{\circ} 40'$ and $68^{\circ} 20' N$ the eastern part of the chain is on Swedish territory, a strip of land more than 800 km long and with a mean width of about 100 km. Between $68^{\circ} 30'$ and $69^{\circ} N$ again a narrow marginal strip is partly on Swedish and partly on Finnish territory. There is no western border of the Scandinavian Caledonides; the rocks that disappear beneath the sea along the west and north coast belong to central parts of the orogenic belt.

Stratigraphy.—Among the sediments of the Caledonian cycle, of Eocambrian and Cambro-Silurian age, it is possible to distinguish distinct types of facies, deposited in different parts of the geosynclinal realm and characteristic of distinct parts of the tectonic succession of nappes.

The deposits of the so-called eastern facies were laid down upon the eastern foreland or in the eastern, miogeosynclinal part of the depositional troughs. Beneath the marine Cambro-Silurian deposits of this facies are the thick, mainly psammitic deposits of the Sparagmite super-group in parts of southern Norway and Sweden and the sandstone and dolomite formations in Finnmark, the northeasternmost part of Norway. Eocambrian is used in Scandinavia as a chronostratigraphical term for the deposits in question. Some geologists consider the younger part of the Eocambrian to be indeed of Lower Cambrian age, while Askund in Sweden has coined the term Varegian for the same part of the sequence. It must be emphasized that Eocambrian deposits are found also in sequences that can not be referred to the eastern facies type, for example, the highly metamorphic psammitic rocks in the west parts of Finnmark.

The marine Cambro-Silurian deposits of the eastern facies are most fully developed in the Oslo region in Norway and in the eastern part of Jemtland

(between 63° and 64° N) in Sweden, as alternating formations mainly of shale, marlstone, and limestone. To the west the amount of calcareous material decreases and there is a corresponding increase in the amount and grain size of the clastic material. Although the rocks are wholly unmetamorphic and richly fossiliferous in the east, they become low grade metamorphic to the west. Volcanic intercalations and typically also Caledonian intrusives are absent in the deposits of the eastern facies type.

A second main type of facies is represented by eugeosynclinal deposits and has been called the western facies. The eugeosynclinal deposits can indeed be referred to two distinct facies, that of the Trondheim region and the Nordland facies. The sediments of the Trondheim region have thick intercalations of basic and also of acid volcanic rocks at various stratigraphic horizons, especially in the Lower and Middle Ordovician. The stratigraphy of the deposits of this facies has been established in the northwest part of the Trondheim region in Norway (district centering about 63° N, 10° E) and in a part of Vesterbotten in Sweden (district centering about 65° N, 15° E), based in each area on a number of fossiliferous formations of Middle Ordovician to Silurian age. In these districts the metamorphism is low grade or almost absent, while in other districts the grade of metamorphism is high. In Sweden the terms Köli and Seve schists are being used for the low-grade and high-grade rocks, respectively. The sediments of the Trondheim region facies contain a multitude of intrusive bodies of varying size, peridotites-serpentinites, gabbros and trondhjemites.

The sediments of the Nordland facies, a sequence of several thousand meters, consist of a lower division mainly of pelites and an upper division with thick limestones and dolomites. Volcanic intercalations are present, but up to the present little is known of their extent and importance. Sedimentary iron oxide ores, found at a number of horizons, are further characteristic. The Nordland sediments are generally strongly metamorphosed, and fossils have never been found in them.¹ But apparently they are in a normal stratigraphic succession above the Eocambrian deposits of western Finnmark.

Great parts of the eugeosynclinal sediments are positively known to form nappes, and there is no reason to believe that any of them are in autochthonous positions. Parts of the Caledonian nappes are built, however, of crystalline rocks of Precambrian (pre-Eocambrian) or unknown age.

The Caledonide nappes.—In most districts the autochthonous Cambro-Silurian is present only as a thin sequence, forming a narrow border zone between the Archean and the overlying nappes and varying in thickness from little or nothing up to about 200 meters, only the Cambrian or, more rarely, the lower part of the Ordovician being represented. The Cambro-Ordovician sequence in the Hardangervidda district in southern Norway (about 60° N, 7° E) must be considered as autochthonous, as it lies in regular succession above the Archean basement. The same is the case with the Cambro-Silurian

¹ The Upper Ordovician or Silurian fossils recently detected in Magerøy, Finnmark, do not seem to be in sediments of the Nordland facies. They are considered to have a stratigraphic and tectonic position similar to the unmetamorphosed Cambro-Ordovician sediments of the Digermul peninsula of the Tana district (Reitan, in Høltedahl, Fjøl, and Reitan, 1960, p. 57).

sequence of the Oslo region, but here as in other districts folding by *décollement* involved a gliding of the sediments above the Archean basement. In Finnmark a thick autochthonous Eocambrian sequence with fossiliferous Cambrian and lowermost Ordovician deposits at the top is found east of meridian 27° E. In the eastern part of Finnmark these rocks are practically unfolded near the border of the Archean.

Very characteristic of the eastern part of the Scandinavian Caledonides are nappes or thrust sheets, which have moved relatively eastward or south-eastward on flat thrust-planes, often very close above the undisturbed peneplaned Archean basement. The nappes are, however, not composed of flat-lying rocks, as in many cases they are known to have schuppen structures.

It may be convenient to divide the nappes in two main groups. In a first group, in a lower tectonic position, are nappes composed of rocks of Eocambrian and Cambro-Silurian rocks of the eastern, miogeosynclinal sequence. In some cases rocks from the Archean substratum of the sediments form parts of the nappes. The lower nappes in the present group, occurring near the Caledonian margin, are unmetamorphosed, while rocks of the higher nappes are metamorphosed and deformed.

In a second group, in a high tectonic position, are nappes composed of sediments of the western eugeosynclinal sequences and of crystalline rocks that in some cases are known to belong to the substratum of the sediments.

Along the Caledonian margin from Hallingdal in Norway (60° 40' N, 9° E) to Vesterbotten in Sweden (about 65.5° N) extends a range of nappes of sandstones of the uppermost part of the Sparagmite super-group (Ringsaker sandstone ("quartz sandstone") in Norway, Vemdal quartzite and Ström quartzite in Sweden). The range of the "quartzite nappes" is interrupted by the Cambro-Silurian district of Jemtland in Sweden.

In the southern part of Vesterbotten (64° 45' N) the Blaik nappe of quartzites and sparagmites with wedges of Archean rocks is considered a western continuation of the Ström quartzite nappe. North of 67° N in Sweden, nappes of Archean rocks are in a similar position as the "quartzite nappes" further south, directly above the autochthonous sediments. The nappes are of rocks similar to those in the Archean substratum ("syenite nappe") and schuppen of the nappe have overlying Cambrian sediments of the same type as in the autochthonous sequence (the "Hyolithes zone"). In Finnmark, between 25° and 27° E, unmetamorphosed Eocambrian sandstones and dolomites form a nappe above the autochthonous sediments along the Caledonian margin; the observed length of the thrust perpendicular to the strike is nearly 30 km.

In the area surrounding the area of the Valdres sparagmite in southern Norway, Cambro-Ordovician phyllites and quartzites of the eastern facies are stratigraphically in a normal succession above the allochthonous Ringsaker sandstone and must thus be in an allochthonous position.

In Jemtland in Sweden, north of 63° N, Cambro-Silurian sediments cover large areas, the greater part of the rocks are allochthonous and form a number of nappes thrust above the autochthonous part. Especially in the Ordovician part of the sequence the upper nappes of western derivation contain

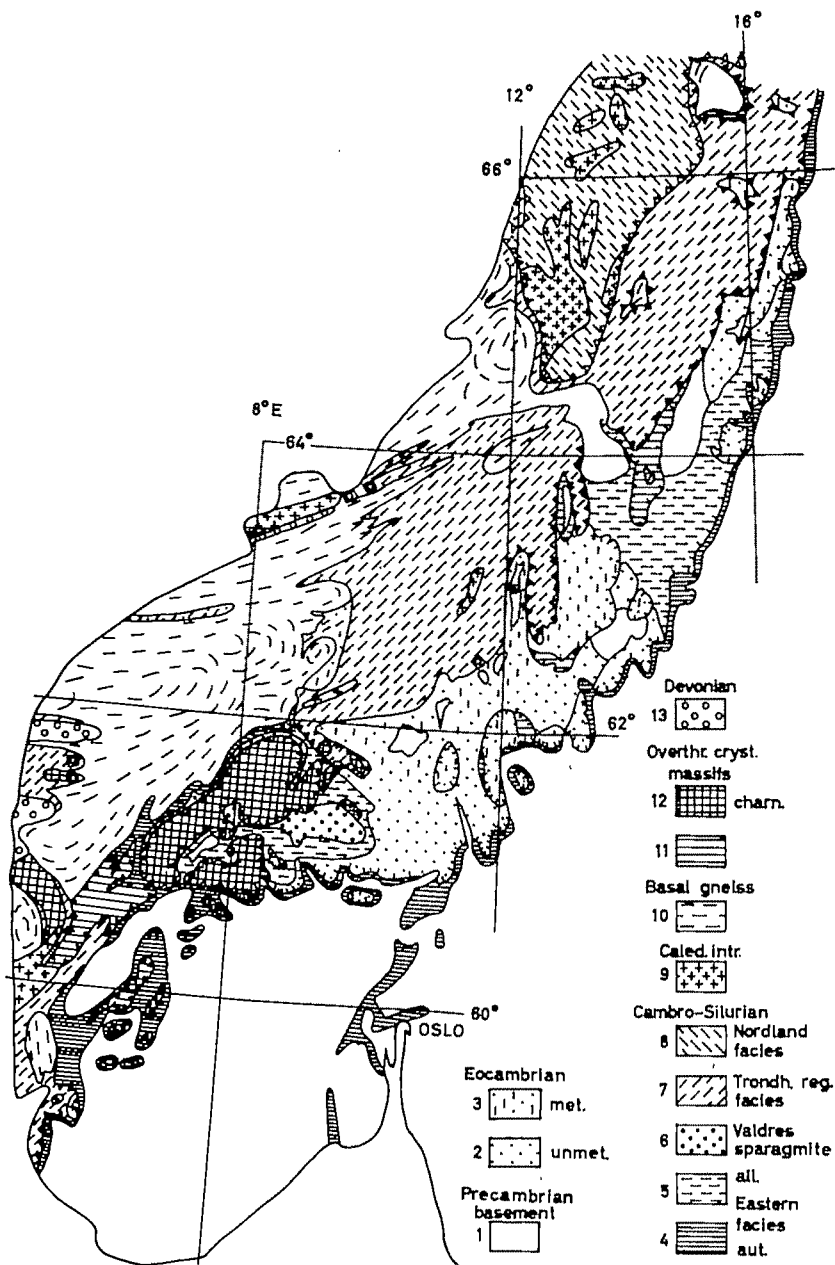
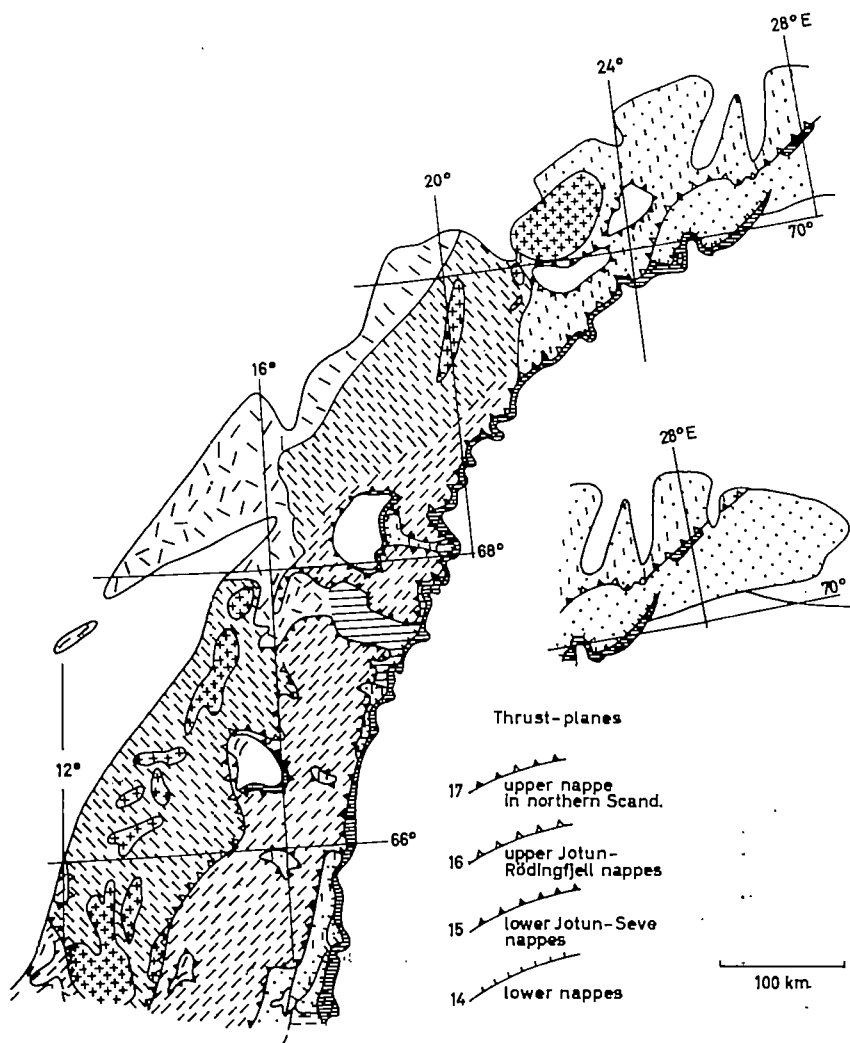


Fig. 1. Geologic-tectonic map of the Scandinavian Caledonides, somewhat schematic and simplified. See explanation on page 166.



less lime and more coarse terrigenous material than do the autochthonous sequence and the lower nappes of eastern derivation. The Offerdal conglomerate, whose stratigraphic position is near the Ordovician-Silurian boundary, may be equivalent to the Valdres sparagmite in southern Norway. The youngest sediments present in the allochthonous sequences are of early Wenlock age.

Next above the "quartzite nappes" are a number of nappes of deformed and metamorphosed Eocambrian sparagmites, quartzites, and dolomites and of strongly mylonitized granitic rocks probably of Precambrian age. The sediments of this group of nappes are intruded by numerous dikes and sills of olivine dolerite ("Ottfjell diabase"), sometimes metamorphosed to chloritic rocks. The rather high degree of metamorphism and the intrusion by magmatic rocks give the nappes of this group a position transitional to the overlying

nappes of eugeosynclinal facies. The Kvitvola nappe in the eastern part of the Norwegian Sparagmite district near the international border (about 62° N., 11 to 12° E) is built mainly by light-colored feldspathic sandstones (called "light sparagmites" in Norway). "Light sparagmites" of similar types have a wide distribution in the northern part of the Sparagmite district of Norway, sometimes metamorphosed into augen-gneisses. Most of these rocks are certainly allochthonous, but it is doubtful whether they all form one tectonic unit together with the Kvitvola nappe. The tectonics of the Sparagmite district presents many unsolved problems.

The Kvitvola nappe continues into Sweden under the name of the Serv nappe and forms a flat-lying sheet about 100 km long in north-south direction south of the 63rd° parallel. The same nappe occurs also further north between 65° and 66.5° N. Beneath the Serv nappe in the southern districts are augen-gneisses, coarse-grained granitic rocks with feldspar augen. Granitic rocks, for the most part strongly mylonitized, build the Offerdal nappe (or "granite mylonite nappe") extending for 150 km to the north-northeast. In the southern parts of Jemtland it rests on allochthonous Cambro-Silurian rocks and carries

Explanation of Figure 1

1. Precambrian basement, Precambrian rocks not affected by Caledonian movements, or at least without any radical change in mineral composition and structure.

2—3. Eocambrian: the Sparagmite super-group and the sandstone-dolomite formations in Finnmark.

2. Unmetamorphosed rocks: the "quartzite nappes" and parautochthonous rocks in the southern and middle districts; the sandstone and dolomite formations of Finnmark (the northeasternmost part of Norway), allochthonous in the west, autochthonous in the east.

3. Metamorphic rocks, all or most of them allochthonous: the Kvitvola-Serv nappes, the Stalon nappe, and the main nappe in western parts of Finnmark.

4—8. Cambro-Silurian.

4. Eastern facies, autochthonous.

5. Eastern facies, allochthonous.

6. Valdres sparagmite, in central southern Norway.

7. Eugeosynclinal Trondheim region facies, probably all the sediments allochthonous, in the lower Jotun nappe in southern Norway and the Seve nappes in Sweden.

8. Eugeosynclinal Nordland facies, in the Rødingfjell nappe in northern Norway.

9. Caledonian intrusive rocks, comprising the gabbros, diorites, trondhjemites, and other rocks of the opdalite-trondhjemite kindred, the granites of Nordland, and also the basic massifs of Lyngen and Finnmark.

10. Basal gneiss, below Cambro-Silurian sediments in the central parts of the orogenic belt, "Caledonized" Precambrian rocks, and Caledonian migmatites.

11—12. Crystalline rocks in the nappes, of Precambrian or unknown age.

11. Schists and gneisses in the nappes of Hardangervidda, metamorphosed supracrustals (with intrusives) in the Bergsdalen nappes, augen-gneisses, and granite mylonites in the Offerdal nappe, "syenite nappe" in northern districts.

12. Charnockitic rocks of the Bergen-Jotun kindred in the lower and upper Jotun nappes in southern Norway.

13. Old Red Sandstone deposits of Lower and Middle Devonian age.

14. Thrust-planes of the nappes of the lower structural unit—sediments of miogeosynclinal facies.

15. Thrust-planes of the lower Jotun and Seve nappes, lower part of upper structural unit—sediments of eugeosynclinal facies.

16. Thrust-planes of the upper Jotun and Rødingfjell nappes, upper part of upper structural unit—sediments of eugeosynclinal facies.

17. Thrust-plane of upper nappe (upper structural unit) in the northern parts of Scandinavia.

an outlier of the Serv nappe on its back. The Stalon nappe, extending between $64^{\circ} 40'$ and 66° N in Vesterbotten, consists of metamorphosed sparagmites and has a position analogous to the Serv nappe.

Turning now to the upper Caledonian nappes with sediments of a eugeo-synclinal facies, we shall first consider the conditions in central southern Norway. A sheet of charnockitic rocks, known as the upper Jotun nappe, here extends 180 km in direction northeast-southwest (the strike direction) and 85 km northwest-southeast (including a gap due to erosion), resting upon underlying sediments. Northeast of this huge nappe, at about $61^{\circ} 50'$ N, 9° E, smaller massifs of the same general type of charnockitic rocks are normally overlain by a sedimentary sequence of the Trondheim region facies. The said charnockitic massifs with their sedimentary cover form a nappe thrust above Cambro-Ordovician phyllites and quartzites of the eastern facies, in parts of the area upon underlying Eocambrian sparagmites. This nappe unit is known as the lower Jotun nappe. The Valdres sparagmite in the central part of southern Norway is a formation chiefly of arkoses (sparagmites) rich in microcline, but including quartzite conglomerates, with an upper division of meta-graywackes rich in albite, epidote, chlorite, and amphibole, indicating a derivation from gabbroid rocks. It can be shown that the Valdres sparagmite contains material from the overthrust charnockitic massifs, from the common occurrence among its feldspar grains of perthites characteristic of these rocks, in some cases even from boulders in its conglomerates. An early Silurian sandstone in the northern part of the Oslo region contains grains of perthites of the same types as those found in the Valdres sparagmite. There is no known source of the perthites in question other than the charnockitic rocks in the overthrust massifs in central southern Norway, which must thus have been moved to their present geological surroundings before the beginning of Silurian time.

The position of the Valdres sparagmite is above the lower Jotun nappe and below the upper Jotun nappe, as has been found everywhere that the three units are found in one and the same section (fig. 2). Thus the *mise-en-place* of the lower Jotun nappe must have been in a Taconic phase before the deposition of the Valdres sparagmite. Judging from fossils found in a number of places, none of the marine sediments below the Valdres sparagmite (and below the nappes) should be younger than early Middle Ordovician. The rocks of the lower Jotun nappe must be assumed to have undergone erosion before and during the deposition of the Valdres sparagmite, and only comparative small remnants of the original nappe are now present. In a later phase the upper Jotun nappe was overthrust above the Valdres sparagmite.

In the Hardangervidda-Rogaland district (about 59.5° N, 7° E) a sheet of gneisses and crystalline schists, greatly dismembered by erosion, forms a nappe above autochthonous Cambro-Ordovician phyllites. In the southwest part of the same district, at the Boknfjord near Stavanger, sediments of the Trondheim region facies and igneous rocks intruded into them are in a similar tectonic position above the phyllites and are probably a part of the same nappe as the gneisses and schists in the areas to the northeast. The sediments of the Boknfjord thus have the same facies as the sediments of the lower Jotun nappe and may be a part of the same tectonic unit.

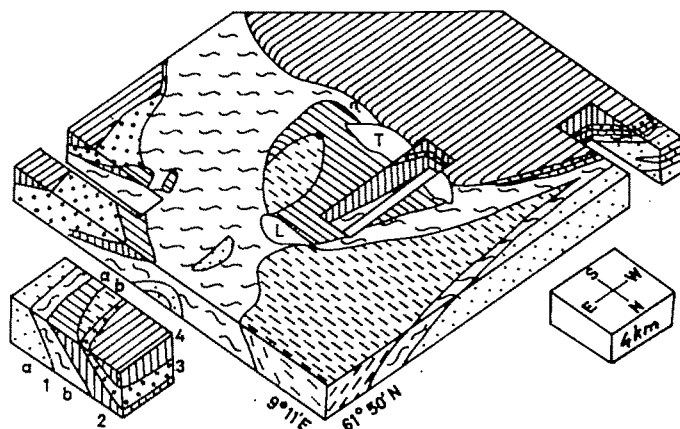


Fig. 2. Tectonogram of a district south of the Otta valley in central southern Norway, to show the relations between the Valdres sparagmite and the lower and upper Jotun nappes. L—Lake Lemonsjøen, T—Lake Tesse.

1a,b. Eocambrian sparagmites and Cambro-Ordovician phyllites and quartzites—sediments of eastern facies below the great nappes.

2a,b. Crystalline basement rocks and sediments of the Trondheim region facies of the lower Jotun nappe.

3. Valdres sparagmite, represented by meta-graywackes rich in albite, epidote, and chlorite, containing boulders of trondhjemites and other rocks—the “Gabbro conglomerate”.

4. Charnockitic rocks of the upper Jotun nappe.

To the southwest of the continuous massif of the upper Jotun nappe and east of the city of Bergen are the Bergsdalen nappes, consisting in all of four sheets of quartzites and volcanic rocks, metabasalts, metadacites, and meta-rhyolites of assumed Precambrian age—with intruded diorites and granites. The Bergsdalen nappes are below the upper Jotun nappe and must thus have been thrust earlier than that large nappe. Further, according to sections recently published by Kvale (1960), the rocks of the Bergsdalen nappes are overlain by sediments and volcanics of the Trondheim region facies occurring southwest of the Bergsdalen rocks at the Hardangerfjord. Might it be that the sediments and volcanics in question form one tectonic unit together with the Bergsdalen nappe? In any case the sediments of the eastern and of the Trondheim region facies occur very near to each other at the Hardangerfjord, and it is a reasonable assumption that the areas of deposition of the two very different facies of sediments were farther apart. It thus seems possible to correlate the Bergsdalen nappes with the lower Jotun nappe.

In the midst of the Bergen arcs (at the west coast between 60° and 61° N) is a massif of charnockitic rocks, underlain at both sides by sediments of the Trondheim region facies. The charnockitic Bergen massif is most probably to be correlated with the upper Jotun nappe, but it is greatly influenced by the movements that led to the formation of the Bergen arc structures. Sediments of the Trondheim region facies are also found below the Devonian deposits north of Bergen.

In southern Norway between 62° and 64° N is the large area of axial depression of the Trondheim region with Cambro-Silurian sediments of the

facies typified in that area. Little is known at present of the tectonics of the Trondheim region, and future research may well show that more than one tectonic unit is present in that large area. In the southwestern part of the region, the sediments are in direct connection with the sediments of the lower Jotun nappe in the northern part of Gudbrandsdalen, while at the eastern side they are in connection with the rocks forming the Seve nappe in Sweden. There is thus no reason to consider the sediments of the Trondheim region to be in an autochthonous or parautochthonous position.

To continue our review of the eugeosynclinal nappes we have to turn to Jemtland in the southern part of the Swedish Caledonides, a classical area of nappe tectonics. It was here that A. E. Törnebohm in the 1880's found the clue to the understanding of Caledonian tectonics and to the solution of the "mountain problem" of the Scandinavian geologists. In the Jemtland region we have already described the "quartzite nappe" of late Eocambrian sandstones, the nappes of Cambro-Silurian sediments of eastern facies, the granite mylonite nappe, and the Serv nappe of metamorphosed light sparagmites. At the top of this tectonic sequence is the large Seve nappe. The eastern and lower part of this large unit consists of the Seve schists: highly metamorphosed and even migmatized schists and gneisses and intrusive rocks, including large masses of amphibolites (in some regions, therefore, the nappe has been called the "amphibolite nappe"). The upper part of the nappe is of less highly metamorphosed sediments, the Köli schists. The difference between the Seve and Köli rocks is considered to be mainly one of different metamorphic grade, though Askund considers that basement rocks of the Köli sediments may be contained in the Seve. As already mentioned, the sediments of the Seve nappe in Jemtland are in connection with the sediments in the Trondheim region at the Norwegian side. Further north in Vesterbotten (about 65.5° N) the stratigraphy of the Seve nappe sediments is established by a number of fossiliferous formations of Upper Ordovician and Silurian age. The Seve nappe has been recognized as far north as Lake Torneträsk (69° N), where the Caledonian margin cuts the national border just north of the lake. In the Swedish Sulitelma district (67° N), the Seve nappe has been shown to consist of three thrust sheets and thus to be a composite tectonic unit.

As indicated on the legend of the map (fig. 1), the Seve nappe has been correlated with the lower Jotun nappe in southern Norway. This may be justified as far as both have a similar position in the tectonic sequence and contain sediments of the same general facies. While there are good indications, at least, that the lower Jotun nappe was moved to its present tectonic position in a Taconic phase, this cannot have been the case with the Seve nappe. The latter in Jemtland has been thrust above fossiliferous Silurian rocks and also contains Silurian sediments. Although it is possible that nappe structures were formed in the Seve nappe in a Taconic phase, as claimed by G. Kautsky, the final *mise-en-place* of the nappe cannot be earlier than late Silurian.

The Rödingfjell nappe is a name given to a nappe of highly metamorphic rocks above the Seve nappe. The nappe was first recognized on Swedish ground, but the main part of the nappe is in Norway; it is built by highly metamorphic sediments of the Nordland facies with numerous granite massifs.

On Norwegian ground the thrust-plane below the Rødingfjell nappe has been mapped as far north as $66^{\circ} 20'$. In the south the outcrop of the thrust-plane of the Rødingfjell nappe bends to the west at $64^{\circ} 20' N$ and continues to the northwest towards Foldenfjord. Northwest of that fjord, at $65^{\circ} N$, $12^{\circ} E$, the massif of the Bindal granite, heavily mylonitized in its lower part, stands up as a wall above underlying micaceous gneisses and meta-basalts; further to the north the thrust-plane disappears below the sea. This interpretation implies a minimum of about 100 km for the length of transport of the Rødingfjell nappe. The Rødingfjell nappe can be correlated with the upper Jotun nappe in southern Norway in so far as both form an uppermost tectonic unit. North of the Sulitelma district ($67^{\circ} N$) a boundary between the Rødingfjell and the underlying Seve nappes has not been determined. Sediments of the Nordland facies, typical of the Rødingfjell nappe, are known to occur in the district just south of Tromsø (at $69.5^{\circ} N$).

In the most northeastern part of the Caledonides large masses, mostly of highly metamorphic rocks, lie overthrust above the autochthonous Cambrian to the southeast and above the unmetamorphosed Finnmark sandstone and dolomites to the east. Future research may show the presence of more than one tectonic unit among the thrust rocks in this large area, only small parts of which have been closely examined until now. East of the 22nd meridian the overthrust rocks consist mostly of metamorphic psammitic rocks containing also tillites and certainly of Eocambrian age. To all appearance they are normally below the mainly pelitic rocks to the west of them, of assumed Cambro-Silurian age. In the northwest parts the psammitic rocks are highly metamorphosed and granitized, parts of the complex consisting of coarse-grained gneisses. In this part of the Caledonides are the large massifs of gabbroid rocks with banded structures in Lyngen and in Vest-Finnmark.

Basal gneisses and basal massifs.—At the southeast margin of the Caledonides there is a very sharply marked unconformity between the Precambrian basement and the overlying Eocambrian and younger sediments. Likewise at the northwestern side of the areas occupied by Cambro-Silurian sediments in southern Norway gneisses underlie the sediments, but here with a perfect conformity. In some districts it is even difficult to find any distinct boundary between the gneisses and the overlying sediments. So far it might be possible to interpret the so-called basal gneisses as Precambrian rocks that had acquired new structures during the Caledonian orogeny. But in some areas sediments of the Caledonian cycle pass into underlying gneiss by an increasing feldspathization of the sediments. Bands of quartzite often accompanied by limestone and lime silicate rock strike through parts of the gneiss area. In one case a quartzite extending at least 50 km out into the gneiss area has been shown to be in connection with an Eocambrian quartzite occurring at the border of the gneiss with the overlying sediments. Further, peridotites occurring as numerous bodies in parts of the gneiss region can in no way be distinguished from the peridotites in the Trondheim region sediments. Thus parts of the gneisses must be migmatites of Caledonian origin. In the Oppdal district west of the Trondheim region basal gneiss and overlying Eocambrian flagstones and Cambro-Ordovician "Trondheim schists" form large folds, sometimes ap-

proaching the Pennine type of tectonics. This type of tectonics is reported also in the districts to the west of the Oppdal district.

In northern Norway a basal massif of coarse-grained granite appears beneath the sediments in the Tysfjord culmination (68° N, 16° E). The Tysfjord granite is similar to Archean granites occurring 20 km to the east in the Rombak window; on the other hand bands of granitic gneiss closely similar to the Tysfjord granite occur in the sediments above the granite basement. The most likely interpretation seems to be that the Archean Tysfjord granite was "rejuvenated" during the Caledonian orogeny. A complex of banded gneisses in the Vesterålen-Lofoten archipelago, west of the Tysfjord culmination, contains inclusions of micaschists, limestones, and sedimentary iron ores. To the west the metamorphic grade increases and reaches the granulite (charnockite) facies, and the said gneisses thus pass into the coarse-grained highly crystalline rocks that give the wild rugged topography to the western Vesterålen and Lofoten islands.

Age of deformation.—Lower and Middle Devonian sandstones and conglomerates of Old Red Sandstone facies occur in southern Norway in two districts at the west coast and in a very small area near the national border at 62.5° N. They lie with profound unconformity above the strongly folded and metamorphosed Cambro-Silurian rocks. In the island of Hitra the age of the unconformity is fixed by the occurrence of *Dictyocaris*, indicating a Ludlowian or Downtonian (uppermost Silurian) age, in the basal part of the sequence above a Caledonian diorite. Thus the main Caledonian orogeny in the central parts of the mountain chain was ended before the beginning of Devonian time. In the Oslo region, a marginal part of the orogenic belt, the folding took place later, as the continental Ringerike sandstone of Ludlowian-Downtonian age is here conformable with the underlying marine sequence, and the folding must be early Devonian or later. A correlation of the phases thus indicated with the Ardennian and Erian phases established in other regions is near at hand. A Taconian phase is strongly indicated in southern Norway. Conglomerates in the Trondheim region sequence indicate disturbances with uplift and erosion between the lower and middle and between the middle and upper part of the Ordovician and between the Ordovician and the Silurian. More than one phase of folding has been proved by painstaking structural studies carried out in a few areas. It is also known that the thrust-planes of the large nappes have been affected by later movements. The movements leading to the formation of the Bergen arc structures (at the west coast of southern Norway) were later than the formation of the nappes but older than the deposition of the Devonian sandstones. Furthermore, the Devonian sediments along the west coast were subjected to rather intense folding and thrusting after deposition. A problem presenting itself is the degree to which the post-Middle Devonian earth movements manifested themselves outside the areas with Devonian sediments. They seem to be restricted to western districts, as the Devonian sediments in the eastern area at Røragen have been tilted but not folded, the tilting being ascribed to faulting, probably of Permian age.

The picture that can be given of the Scandinavian Caledonides is an incomplete one, as the western part of it and its western foreland is now beneath

the sea. Marginal faults along the Norwegian coast have been assumed by O. Høltedahl on the basis of study of submarine topography.

The Scandinavian Caledonides have all the attributes of a fully developed orogenic belt: strong volcanism occurred in the geosynclinal phase, large sheets of sediments and even of the underlying basement were cut out and moved as nappes for distances of 200 km or perhaps even more, and plutonic processes led to magmatism and strong metamorphism and migmatization. Probably no other part of the world shows a stronger manifestation of Caledonian orogeny. Perhaps as a consequence of this, the later history of Scandinavia is mainly one of vertical uplift and fracturing (exception being made for some marginal districts). This is in contrast to the Caledonian regions in the British Isles and in Spitzbergen, which show a rich history of late Paleozoic and younger subsidence and sedimentation.

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DIFFERENTIATION TRENDS IN THE ICE RIVER COMPLEX, BRITISH COLUMBIA

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ABSTRACT. Four phases of the complex (jacupirangite, ijolite, nepheline syenite, and sodalite syenite) were studied from the viewpoint of their chemical variation. If one goes from the first-formed jacupirangite to the last-formed sodalite syenite, CaO , FeO , Fe_2O_3 , MgO , and TiO_2 decrease, whereas SiO_2 , Al_2O_3 , Na_2O , K_2O , and volatile content increase.

A tentative diagram for the system $\text{SiO}_2\text{-NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8$ at a water pressure of 1000 kg/cm^2 is used to study the differentiation path. Jacupirangite lies well above the diagram due to its high CaO and MgO content. Ijolite is at or near the liquidus of the system, and nepheline syenite falls in the cotectic trough between the feldspar and nepheline fields. Sodalite syenite does not appear to lie at the ternary eutectic in the position expected of the last differentiate.

GENERAL STATEMENT

The Ice River complex (fig. 1) was first referred to by Dawson (1885). Subsequently certain rocks from the body were studied by Barlow (1902) and Bonney (1902). Allan (1914) spent the seasons of 1910 and 1911 in the Field map area and conducted a thorough study of the complex. Since that time petrology has made great advances with the elaboration of the reaction principle by Bowen (1922) and the construction of many phase diagrams by personnel at the Geophysical Laboratory in Washington. This paper deals with some chemical variations in the complex and applies the chemical data to a modification of the system $\text{SiO}_2\text{-NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8$.

As shown on figure 2 the complex consists of two separate masses. The larger one trends northwest for about 10 miles. The northwesterly arm of this body shows a width of one mile whereas the southeasterly portion assumes a stocklike aspect and is 5 miles across. The smaller body lies east of the larger and covers an area of 2 square miles. In general it may be said that the body has the intrusive relations of a deformed laccolith (fig. 2). According to the surface exposures, the complex consists of 50 percent nepheline syenite, 40 percent ijolite, 10 percent jacupirangite, and a trace of sodalite syenite.

The intrusive rocks cut the Middle Cambrian Ottertail formation and the Goodsir formation of Cambro-Ordovician age. Mica (lepidomelane) from the body has been dated by the potassium-argon method and yields a Paleozoic date of 350 million years (Baadsgaard, Folinsbee, and Lipson, 1959).

CHEMICAL COMPOSITION

Field relations indicate that the complex consists of a sequence of rocks ranging from a pyroxene-rich early phase to the last-formed sodalite syenite. From this sequence four rock types have been chosen as representing successive stages in differentiation. They are in order from first- to last-formed: jacupirangite, ijolite, nepheline syenite, and sodalite syenite (Allan, 1914). The chemical analyses of these four rock types are shown in table 1, and the data are plotted on a variation diagram in figure 3.

TABLE 1
(Weight percent)

	1	2	3	4	5	6
SiO ₂	35.20	41.66	53.42	54.62	48.80	48.8
TiO ₂	4.06	1.95	0.60	0.04	2.19	1.0
Al ₂ O ₃	13.54	22.75	21.04	22.05	13.98	22.9
Fe ₂ O ₃	3.74	2.33	1.74	0.46	3.59	2.0
FeO	10.36	6.08	2.83	0.32	9.78	4.0
MnO	0.20	0.14	0.07	0.01	0.17	—
MgO	9.60	3.11	0.61	0.05	6.70	1.6
CaO	14.49	7.76	2.88	0.74	9.88	4.7
Na ₂ O	2.61	8.81	7.80	10.12	2.59	9.4
K ₂ O	1.85	3.12	7.48	7.51	0.69	5.6
P ₂ O ₅	1.96	0.10	0.10	0.03	0.33	—
H ₂ O ⁻	0.01	0.03	0.04	0.04	1.80	—
H ₂ O ⁺	1.28	1.50	0.76	0.72	—	—
Cl	0.14	0.02	0.10	2.08	—	—
SO ₂	—	0.045	0.06	1.48	—	—
S	0.43	0.08	tr.	—	—	—
CO ₂	1.51	0.40	0.43	0.87	—	—
Sum	99.98	99.88	99.96	101.12	—	—
Cl≡O	0.03	0.01	.02	.47	—	—
S≡O	0.21	.04	—	—	—	—
Total	99.74	99.83	99.94	100.65	100.00	100.00

1. Jacupirangite (University of Alberta Rock Analysis Laboratory, Edmonton, Alberta, Alex Stelmach, analyst).
2. Ijolite (Allan, 1914, p. 150).
3. Nepheline syenite (Allan, 1914, p. 136).
4. Sodalite syenite (University of Alberta Rock Analysis Laboratory, Edmonton, Alberta, Alex Stelmach, analyst).
5. Basalt, average of 43 analyses (Daly, Larsen, and LaForge, 1942, p. 2).
6. Hypothetical rock from Ice River Complex containing 48.8 percent SiO₂. Data taken from variation diagram.

The variation diagram (fig. 3) presents an opportunity for studying the trends in these silica-poor rocks. It has been noted (Bowen 1928, p. 123) that the curves for the various oxides require very little smoothing in passing from basalts (about 50% SiO₂) through andesites and dacites to rhyolites (about 74% SiO₂). On the other hand, rocks that may be formed by crystal-sorting processes, such as anorthosites, peridotites, and pyroxenites, show a scattering of points. Furthermore, aphanites appear to give the best curve for the liquid line of descent, whereas rocks with increasing proportions of phenocrysts produce points that are more scattered about the curve (Bowen, 1928, p. 118). Figure 4 shows the average liquid line of descent in aphanites in the subalkalic range as well as the deviations of the sorted rocks. In figure 3, the points for the oxides fall on either side of the curves, and this is thought to be due to the deviation of the rocks from an aphanitic texture.

In general, the trends shown by the oxides in the alkalic rocks of the Ice River complex are similar to those found in subalkalic sequences. It is notable that the rocks show an increase in SiO₂ in going from early to late in the complex. The femic oxides FeO, Fe₂O₃, CaO, MgO, and TiO₂ all show a decrease with increasing SiO₂. The Al₂O₃ increases to maximum at about 48 percent

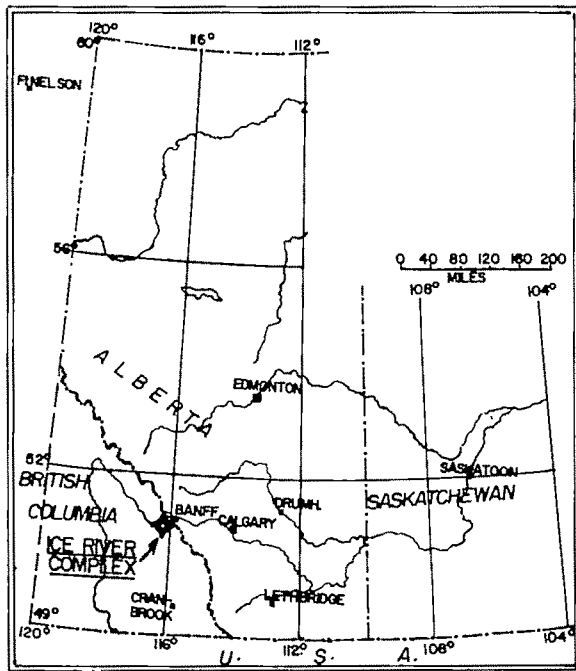


Fig. 1. Location of the Ice River Complex.

SiO_2 and then decreases with increasing SiO_2 . The Na_2O shows a tendency to reach a maximum at 48 percent SiO_2 . The K_2O shows a straight line increase with increased SiO_2 . The K_2O and Na_2O curves if projected will cross at about 57 percent SiO_2 . This intersection in subalkalic rocks occurs at SiO_2 contents somewhat greater than 62 percent. The volatile constituents (H_2O , Cl , S , and SO_3) gradually decrease to a minimum at 50 percent SiO_2 and then increase sharply in the sodalite syenite.

Although the trends are similar to those in subalkalic rocks, the percentages of the various oxides are quite different in this alkalic sequence. In subalkalic rocks the SiO_2 ranges from about 48 to 74 percent, while in the Ice River rocks the SiO_2 goes from about 35 to 55 percent. For purposes of comparison a basalt with 48.8 percent SiO_2 is included in table 1. A hypothetical rock in the Ice River complex with 48.8 percent SiO_2 (number 6, table 1), would lie between ijolite and nepheline syenite on the variation diagram. By comparing the composition of the hypothetical rock with the basalt it is evident that the complex contains very large amounts of Al_2O_3 , Na_2O , and K_2O , and small amounts of Fe_2O_3 , CaO , and MgO . Even so, the fact that the oxides of successive rock types in the complex, when plotted against SiO_2 -content, form liquid descent curves similar to subalkalic rocks indicates that the familiar processes of differentiation were operative.

APPLICATION TO THE SYSTEM SiO_2 - NaAlSiO_4 - KAlSiO_4

Since the equilibrium diagram of the $\text{SiO}_2(\text{Qz})$ - $\text{NaAlSiO}_4(\text{Ne})$ - $\text{KAlSiO}_4(\text{Ks})$ was completed (Schairer and Bowen, 1935; Schairer, 1950), it

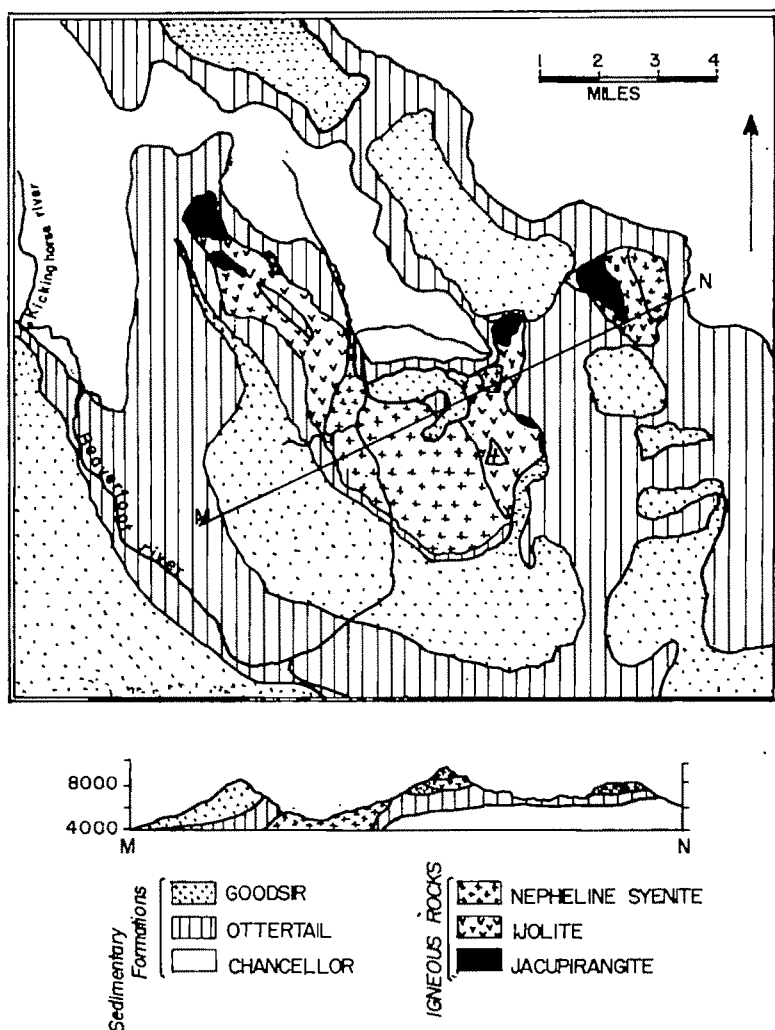


Fig. 2. General geology of the Ice River Complex (after Allan, 1914).

has been most useful in interpretation of natural rocks. The $\text{NaAlSi}_3\text{O}_8(\text{Ab}) - \text{KAlSi}_3\text{O}_8(\text{Or}) - \text{SiO}_2(\text{Qz})$ portion of the system under various water pressures has been used in a discussion of the origin of granites (Tuttle and Bowen, 1958, p. 54). Tilley (1952, 1954, 1958) has studied the alkaline rocks that lie in the Ab-Or-Ne-Ks portion of the diagram and has indicated some interesting relations between coexisting nephelines and feldspars in volcanic, plutonic, and metamorphic assemblages. From work already done it is evident that this residual system will aid greatly in understanding the rocks associated with both the granite sink and the alkalic sink (fig. 5).

The system at a water pressure of 1000 kg/cm^2 (fig. 5) is more realistic than the dry system for the high-volatile rocks of the Ice River complex. Since

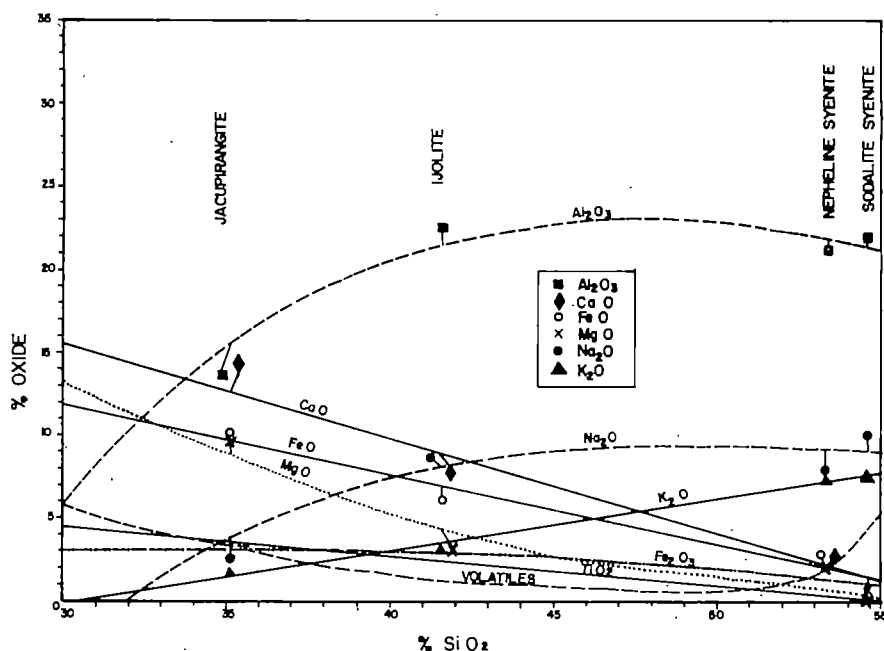


Fig. 3. Variation diagram of four rock types from the Ice River Complex (in weight percent).

only the portion of the system between SiO_2 and the feldspar join has been worked out at this water pressure, the diagram below this join must be considered as only a crude approximation. The norms of the four rock types under consideration were calculated using the procedure given by Johanneesen (1939, p. 88), and these are shown in table 2. For the purpose of plotting on the ternary diagram, the minerals containing K_2O , Na_2O , Al_2O_3 , and SiO_2 were recalculated in terms of Ne, Ks, and Qz and multiplied by a factor to give a sum of one hundred.

TABLE 2

Jacupirangite	Ijolite	Nepheline Syenite	Sodalite Syenite
Lc 8.28	Lc 14.39	Or 44.48	Or 44.48
Ne 11.93	Ne 39.91	Ab 11.53	Ab 29.34
An 19.74	An 15.57	Ne 29.54	Ne 9.37
Di 13.44	Di 16.17	Di 8.40	An 3.89
Ol 19.90	Ol 6.29	Mt 2.55	Co 3.37
Cs 6.71	Cs 1.72	Il 1.22	Hi 3.51
Mt 5.34	Mt 3.25	Ap 0.31	Th 3.41
Il 7.60	Il 3.65	Cc 1.00	Nc 2.12
Ap 4.34	Th 0.71		Hm 0.48
Cc 0.30	Cc 0.90		
$\text{Ne}_{20.5}\text{Ks}_{20.7}\text{Qz}_{11.8}$	$\text{Ne}_{72.2}\text{Ks}_{19.4}\text{Qz}_{8.2}$	$\text{Ne}_{42.8}\text{Ks}_{50.5}\text{Qz}_{7.7}$	$\text{Ne}_{30.5}\text{Ks}_{50.5}\text{Qz}_{19.4}$
Factor x4.95	Factor x1.86	Factor x1.18	Factor x1.20

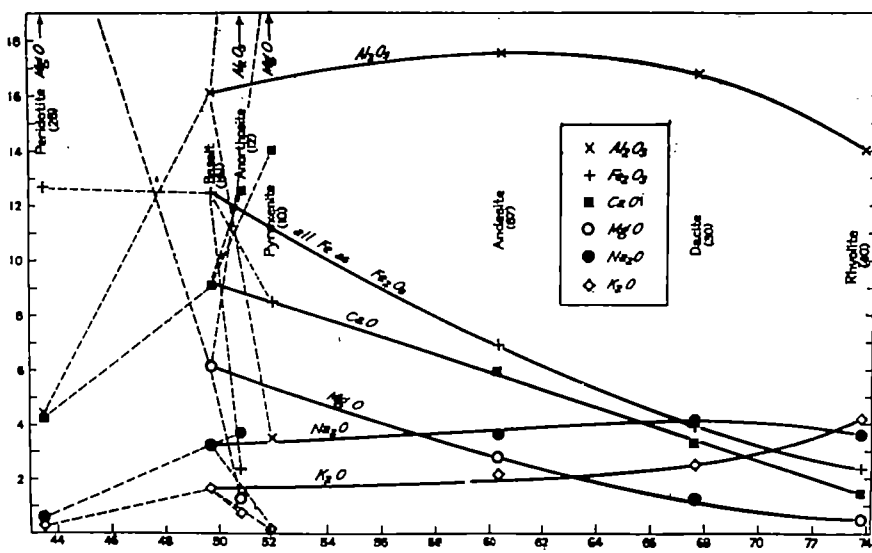


Fig. 4. Variation diagram for Daly's average basalt, andesite, dacite, and rhyolite (solid lines). Broken lines show relation of peridotite, pyroxenite, and anorthosite (after Bowen, 1928, p. 123).

The closer the multiplication factor is to unity the closer the rock type comes to falling in the system under consideration. The points for jacupirangite (J), ijolite (I), nepheline syenite (N.S.), and sodalite syenite (S.S.) are shown on figure 3.

A representative modal analysis of the jacupirangite indicates 75 percent pyroxene, 15 percent magnetite, and 10 percent nepheline. Both from this information and from the factor of 4.95 required to project the data onto the diagram, it is evident that the field of stability for the minerals in this rock lies well above the diagram. The composition of jacupirangite could be plotted better in a tetrahedron with anorthite and diopside at the apex over the system Ne-Ks-Qz. For this reason the liquid trend from J to I must be thought of as a projected line of descent from above the diagram. Ijolite is composed of 50 percent nepheline, 8 percent feldspar, 6 percent sodalite, 30 percent ferromagnesians, and 6 percent other minerals. This rock type is virtually in the plane of the system, and the great abundance of euhedral nepheline indicates the liquid has entered the stability field of this mineral as shown on the diagram.

The liquid then changes in composition and moves down toward the cotectic trough to nepheline syenite. Nepheline syenite gives a modal analysis of 55 percent feldspar, 22 percent nepheline, 7 percent sodalite, 13 percent ferromagnesians, and 3 percent other minerals. The significant thing about this rock is the appearance of large feldspar crystals. The feldspar is often in laths over an inch long and shows Carlsbad twins and perthitic texture. A tie line between the Ab-Or join and the Ne-Ks join, taken in a direction indicated by MacKenzie (1955) and Tilley (1954), would give proportions of 1 nepheline to 2 feldspars, a ratio very close to that actually found in the nepheline syenite.

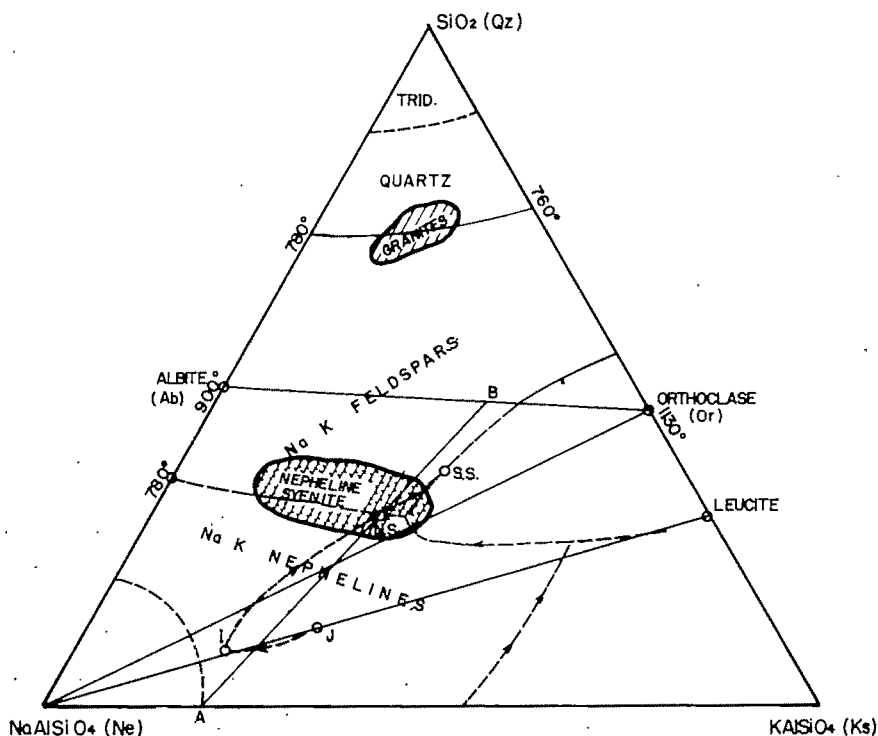


Fig. 5. The system $\text{NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8\text{-SiO}_2$ at water pressure 1000 kg/cm². The regions of granites and nepheline syenites are indicated. The plots of the jacupirangite (J), ijolite (I), nepheline syenite (N.S.), and sodalite syenite (S.S.) are shown. The proposed liquid line of descent is shown by the dashed line and arrows between the four rock types. A-B is a possible tie line between the Ab-Or join and the Ne-Ks join (MacKenzie, 1955).

The behavior of the sodalite syenite poses a problem. A modal analysis shows the rock consists of 60 percent feldspar, 30 percent sodalite, and 10 percent ferromagnesians. The field relations indicate that this rock is very late stage and may even be pneumatolytic (Allan, 1914), as it veins the nepheline syenite and, in places, the sediments. If the sodalite syenite is a late-stage differentiate and the system as shown on the diagram is reasonably correct, then the sodalite syenite should fall in the minimum sink to the right of the nepheline syenite. As seen in figure 5 this is not the case, as it appears to go up the thermal gradient along the leucite-feldspar cotectic. It may be that the extreme volatile content of the sodalite syenite removes it substantially from the system, or what appears more likely, the late veining by sodalite may represent extreme disequilibrium and make comparison with this system invalid.

CONCLUSIONS

The successive rocks in the Ice River complex have had a cooling history that would be expected of a magma undergoing differentiation. The analyses indicate that the magmas from which the rocks formed were of unusual com-

position. The first rock to form was jacupirangite and it contains nepheline as the only salic constituent. Next ijolite formed, bearing abundant nepheline. When the liquid composition entered the cotectic trough between the feldspar and nepheline fields, abundant feldspar appeared as seen in the nepheline syenite. The nepheline syenite was veined by sodalite after the major part of the complex had solidified, and therefore the sodalite syenite should be considered a hybrid rock rather than a late-stage differentiate.

ACKNOWLEDGMENTS

The writer has drawn from the outstanding pioneer work of J. A. Allan (1914). Material in his report on the Field map area and his original samples and thin sections have been used in this study. The study was assisted by a University of Alberta General Research grant.

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THE BASEMENT ROCKS OF MALAYA AND THEIR PALEO GEOGRAPHIC SIGNIFICANCE IN SOUTH-EAST ASIA

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ABSTRACT. In northeastern Malaya a north-south-trending belt of schists of amphibolite facies of apparently anticlinal form is overlain unconformably to the east and west by Carboniferous sediments. It is suggested that these schists are of Precambrian age and represent a remnant of a north-south axis which was active during the Paleozoic. The control of this axis on the paleogeography of Malaya appears to have been very great up to the end of the Devonian.

INTRODUCTION

The most recent geological map of Malaya, which was published in 1948 (Ingham), does not record any metamorphic rocks. The northeastern state, Kelantan, is shown on the map, composed to the west of Carboniferous shales and quartzites with scattered outcrops of volcanic rocks. To the east these are overlain by Triassic shales and sandstones.

The tropical conditions of vegetation and weathering limit accessible outcrops to the courses of rivers. Along the Sungei Galas river, between Dabong and Kuala Krai, a belt, 9 miles wide, of regionally metamorphosed rocks outcrops. It trends north-south. The river section is at right angles to the strike, and the contacts with the Carboniferous sediments to the east and west are sharp and apparently unconformable. Figure 1 shows the position of the outcrop; the extensions to the north and south are inferred.

It seems that the existence of these metamorphic rocks has been known to the Geological Survey of Malaya for some time, but rather oddly they were completely omitted from the published map, for the reason that they were thought to be metamorphosed Carboniferous. To the writer's knowledge, no published reference to this metamorphic belt exists. Alexander (1959), the present director of the Geological Survey, summarized the pre-Tertiary stratigraphic succession of Malaya but made no mention of this metamorphic belt.

It is hoped that this article will satisfy a need of long standing. An attempt is made here to describe briefly the petrology of the rocks and their grade of metamorphism. Time spent in the locality did not permit a detailed structure analysis, but it is hoped that this can be done in the near future.

Scrivenor (1931) believed that the sedimentary formations in Malaya were limited to the range Carboniferous-Permian-Triassic. In 1955-1956 positive identification of Ordovician-Silurian fossils in northwestern Malaya, in the state of Perlis, and of Cambrian fossils in the Siamese island of Terutau, in rocks which are correlatable with those in the Malayan islands of Langkawi, has shown that the range of Malayan stratigraphy does in fact extend from late Cambrian. Jones (1959) mentions a later discovery of Ordovician-Silurian graptolites in the state of Perak in the Kinta valley. A more recent discovery of rocks of the same age has been made in the state of Selangor at Kuala Lumpur. The localities of positive identification of lower Paleozoic are indicated on figure 1.

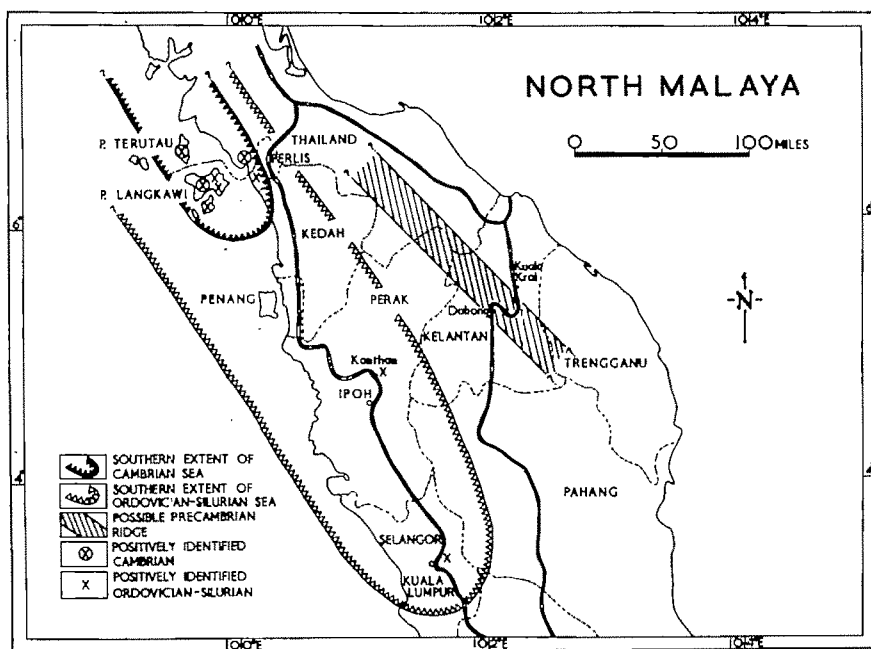


Fig. 1. Paleogeographic map of South-East Asia showing the southern extents of the Cambrian and Ordovician-Silurian seas and their relationship to the Precambrian basement ridge. Devonian is entirely absent from the area.

In view of the parallelism of the extensions of the Cambrian and of the Ordovician-Silurian outcrops with the metamorphic belt which lies immediately to the east, it appears that the latter has had a control on Paleozoic sedimentation, and therefore the writer is of the opinion that it is of Precambrian age. Further weight is given to this thesis on the basis of metamorphic grade. There are several localities of Tertiary metamorphism in Malaya but always of low grade—phyllite grade on the east coast and one isolated metamorphic aureole around the granite of Kedah Peak, which is of biotite grade. However, as will be demonstrated, this belt of regionally metamorphosed rocks in Kelantan is of amphibolite grade. It is unique in this respect and is not obviously associated with the granites. It is pre-Carboniferous and, as the known lower Paleozoic rocks are entirely unmetamorphosed, it seems logical to deduce a Precambrian age.

PETROLOGY OF THE BASEMENT

The rocks are well exposed along the Sungai Galas river, the more resistant bands giving rise to a series of rapids. The complex is largely of garnetiferous mica schist with occasional psammitic bands. Of particular interest is the western part of the succession, which is of amphibolite facies, containing epidote, andesine feldspar, rare garnet, and pyrite. The structure of the complex appears to be anticlinal. To the east the foliation dips to the east, but upstream the dip changes to the west. Only the amphibolite grade schist is described fully here because of its unique position in Malayan geology.

A modal analysis of the amphibolite gave the following results:

Hornblende, 61.2% by volume. Deduced composition $H_2Ca_2Mg_3Fe_2Si_8O_{24}$.

Feldspar, 25.3% by volume. Deduced composition $Na_3Ca_2Al_7Si_{13}O_{40}$.

Clinozoisite, 11.2% by volume. Deduced composition $H_3Ca_2Al_8FeSi_9O_{39}$.

Garnet, 1.7% by volume. The crystals were too small for successful separation and are always intimately associated with the epidote.

Pyrite, 0.6% by volume.

Taking only the three principal constituents, the chemical composition was deduced and is given below.

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O
Weight %	53.6	9.9	0.7	10.5	nil	8.8	13.3	1.6	nil	1.6

A = 11.2%; C = 34.8%; F = 54%.

The position of this rock, using the deduced chemical composition, is shown on the ACF diagram of figure 2. It is seen to belong to the Vogt amphibolite facies, staurolite-kyanite subfacies, which for a rock with a high CaO:Na₂O ratio will cause the appearance of epidote in the normal plagioclase-hornblende-almandine schist.

Wiseman (1934) recorded epidiorites of identical mineralogy to the Kelantan rock from the Garnet and Kyanite zones. A possible igneous origin is further supported by the similarity of the deduced chemical composition to that of basalt.

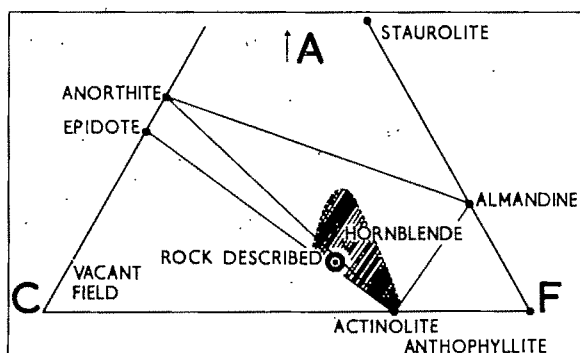


Fig. 2. Amphibolite facies, staurolite-kyanite subfacies. ACF diagram for rocks with excess SiO₂ and deficient in K₂O. (After T. Vogt). The position of the Malayan amphibolite is shown. Note that in rocks low in Na₂O, epidote may be, as in this case, associated with plagioclase.

CONCLUSION

It is suggested that the metamorphic rocks of northeastern Malaya are of Precambrian age for the following reasons: (a) They are unconformably overlain by Carboniferous sediments. (b) They have been metamorphosed to a considerably higher grade than any rocks of Cambrian or later age. (c) Their mineralogy suggests an igneous origin. They must therefore have been em-

placed before the main Tertiary orogeny that was responsible for any other known metamorphism in Malaya.

PRE-DEVONIAN PALEO GEOGRAPHY

Precambrian basement.—Archean Mongkok gneisses form a belt, 12 miles wide, in Burma, trending north-south along the edge of the southern Shan Plateau, and run into the sea to the south at Moulmein (Chhibber, 1934). These are of sillimanite-bearing garnetiferous biotite gneiss with associated igneous intrusions. They have been correlated with the charnockitic Archean gneisses of South India. The Burmese Precambrian is on the same strike as the Malayan basement ridge described here.

Extrapolating this trend to the south, it would cut across western Sarawak and west and central Borneo. In Sarawak, Wilford (1955) has recorded a basement of hornblende-plagioclase schist, which is staurolite bearing in places, in the extreme west tip of that country. They are definitely pre-Permian, but their lower age limit is unknown. Van Bemmelen (1949) has noted a basement of crystalline schists derived from igneous rocks, mainly of basic composition, occurring extensively in west Borneo in a north-south-trending axis which swings eastward towards the south. He believes that some of these may be older than Permian. Similarly, Reinhard and Wenk (1951) have recorded remnants of a metamorphic basement of amphibolite facies, in north Borneo, around Darvel Bay.

It seems therefore that along a north-south axis extending from Burma, through Thailand and Malaya, into Sarawak and swinging east through Borneo into north Borneo is a zone of isolated remnants of a basement which in Burma has been definitely proved to be of Precambrian age. It is therefore reasonable to assume that the Malayan schists are part of this basement and are correlatable with the Precambrian of Burma.

Cambrian.—Rocks of possible Cambrian age are very extensive in Burma, grouped under the name "Mergui Series", and forming a belt which runs southwards into Thailand at Victoria Point. The series is predominantly argillaceous and is overlain by fossiliferous Ordovician. Cambrian has been positively identified on the Thailand island of Terutau (Alexander, 1959) in rocks which are easily correlated with the argillaceous Phuket series of Langkawi and North Perlis (fig. 1). No Cambrian exists to the south of north Malaya.

Ordovician-Silurian.—The Pindaya beds of the Southern Shan States of Burma are of Ordovician age. They are overlain by a series which contains graptolites of Valentian age. Jones (1959) has recorded graptolite-bearing rocks of the same age in the northeastern part of the Langkawi islands of Malaya and in west Perlis, and more recently in the state of Perak at Kanthan. A more southerly, but yet unpublished, discovery of graptolite-bearing Ordovician-Silurian has recently been made at Kuala Lumpur. No rocks of similar age exist to the south of Malaya.

The southerly extents of the Cambrian and Ordovician-Silurian seas can be constructed with a fair degree of certainty and are shown in figure 1. Devonian, although present in Burma as the Plateau Limestone, is absent in Malaya and to the south. It is obvious from the paleogeographic map (fig. 1)

that the basement ridge of Kelantan has had a strong influence on the southern extensions of the lower Paleozoic seas. It has tended to present a positive axis which has gradually subsided during the Cambrian into the Ordovician and through the Silurian, but which has emerged again in the Devonian to cause the complete retreat of the sea to the north.

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ORIGIN OF ALBITE IN GRANITIC ROCKS

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ABSTRACT. Albite in granites commonly occurs adjacent to potassium feldspar, either as rims on oligoclase or as small scattered grains. The albite was not derived either from adjacent potassium feldspar or from more calcic plagioclase and appears to have formed roughly synchronously with the potassium feldspar. Consequently, the albite appears to be a product of direct crystallization during the later stages of magmatic solidification.

INTRODUCTION

The genetic significance of granitic textures has been a subject of controversy for some time. Many of the arguments concerning the "granite problem" devolve about the interpretation of porphyritic, graphic, or other textures. The classical explanation of the various features as resulting from sequential crystallization of a magma followed by minor deuteric reactions has recently been challenged by magmatists as well as granitizationists. For example, recent papers by Tuttle (1952) and Tuttle and Bowen (1958) advocate a general magmatic origin for granites but stress the importance of postsolidification recrystallization to account for many of the textures shown by the alkali feldspars.

The object of the present paper is to examine some of the properties of the minor fine-grained albite and myrmekitic albite which occurs in addition to the "normal", coarser-grained, plagioclase (generally oligoclase) in many granitic rocks. This albite generally occurs as small grains around the borders of potassium feldspar (fig. 1) or as distinct oriented rims on the more calcic plagioclase grains where they are in contact with potassium feldspar (fig. 2). The albite, whether myrmekitic or not, is generally regarded as "secondary" in the sense that it has formed by recrystallization, replacement, or some other process after the major process of formation of the solidified granite. In contrast to the concept of secondary origin, the present paper attempts to demonstrate that much of the albite in granitic rocks has formed simply as a late-stage crystallization product of a granitic melt. In order to reach this conclusion, it will be necessary to demonstrate that the albite has been derived from a fluid phase and that it has formed synchronously with the associated potassium feldspar.

The terminology used in this paper is as follows: (1) fine-grained albite refers to tiny, separate, unoriented grains; (2) rim albite refers to albitic rims on more calcic plagioclase grains; (3) the major portion of the plagioclase in granites occurs as relatively large, commonly subhedral, grains with a composition in the oligoclase range and will be referred to as normal plagioclase; (4) myrmekite signifies any intergrowth between quartz and plagioclase; and (5) graphic signifies any intergrowth between quartz and potassium feldspar. Most of the albite in granites is in the range of $Ab_{100}-Ab_{95}$.

A thorough review of the literature concerning myrmekite up to 1948 has been given by Drescher-Kaden (1948), and many of his citations necessarily deal with albite in general. Textural features of alkali feldspars are thoroughly

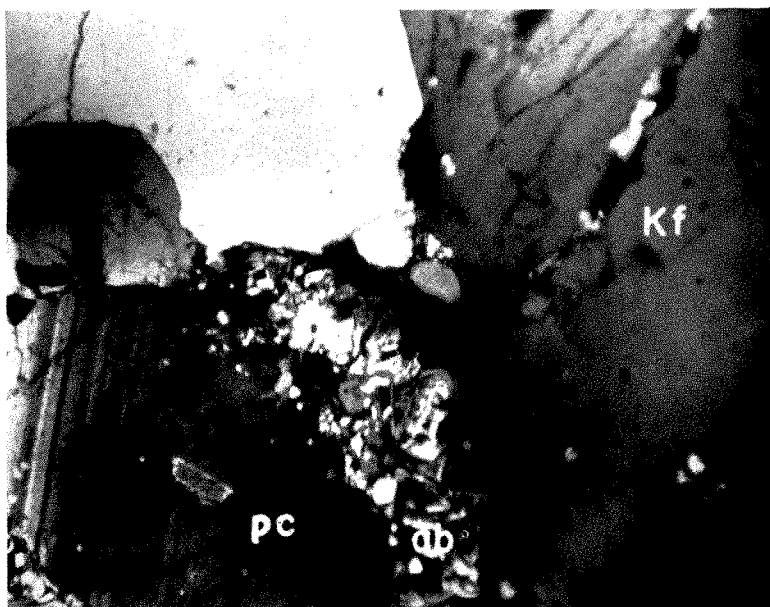


Fig. 1. Fine-grained albite (ab) along the border between plagioclase (pc) and potassium feldspar (Kf). Note the absence of albite along other borders such as plagioclase-quartz (q) and quartz-potassium feldspar. Some of the fine-grained albite is myrmekitic. The sample is from the outer facies of the Idaho batholith. Crossed polarizers, X 75.

discussed in the two papers by Tuttle and Tuttle and Bowen cited above, and in a recent paper on the Enchanted Rock batholith, Hutchinson (1956) describes a number of intricate relationships between potassium feldspar and sodic plagioclase. Robertson (1959) describes some perthitic and other feldspar textures resulting from general potash metasomatism.

ACKNOWLEDGMENTS

The writer expresses his thanks to Dr. Richard Pliler for his advice in the preparation of this paper. All of the samples were collected by Dr. J. M. Whitfield in the summer of 1956. This paper has resulted from work done on granitic rocks in connection with a general investigation of the geochemistry of thorium, which is supported by Grant C-009 from the Robert A. Welch Foundation.

SOURCE OF ALBITE

If the albitic plagioclase in granites has formed by simple recrystallization and other readjustment after solidification of the rock, it has presumably been derived either from the potassium feldspar or the more calcic normal plagioclase with which it is generally associated. If the albite has not been derived from either of these two minerals, then the most readily apparent or plausible source is some fluid phase.

Two observations demonstrate that the albite has not been derived from the normal plagioclase grains. First, if derived in such manner, there is no

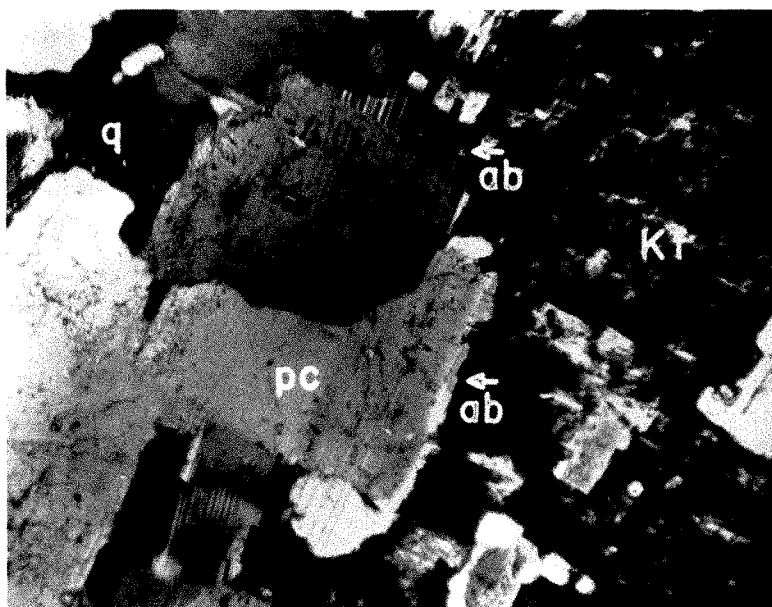


Fig. 2. Rim albite (ab) on the margins of plagioclase grains (labeled pc or showing albite twinning) adjacent to potassium feldspar (Kf). Note the absence of albite on plagioclase-quartz (q) and plagioclase-plagioclase borders. The sample is from the Taft granite of the Yosemite area. Crossed polarizers, X 75.

conceivable reason why the albite should not completely surround the plagioclase either uniformly or randomly; in actual fact, albite occurs only along those borders in contact with potassium feldspar (fig. 2), as is documented by Tuttle (1952). Second, normal plagioclase grains partially surrounded by the albite generally have a uniform composition or exhibit a symmetrical normal zoning outward from the center. Loss of albite from a grain should result either in reverse zoning or in some irregular compositional variations within the grain.

The more plausible argument that the albite is derived from potassium feldspar fails to answer two other observations. First, much of the fine-grained albite around the borders of potassium feldspar and as rims on normal plagioclase grains is myrmekitic. Albite which occurs as rod and film perthite formed by exsolution, however, is rarely, if ever, myrmekitic. It seems likely, then, that if undoubted exsolution does not produce myrmekite, the myrmekitic albite has not formed by that process. Further support for this contention is found in the fact that albitic rims around normal plagioclase inclusions in potassium feldspar (fig. 3) are rarely myrmekitic, and they have quite likely formed by exsolution from the potassium feldspar.

A second argument against the derivation of the albite from potassium feldspar is that in such a process the albite should be distributed uniformly or randomly around the margins of the potassium feldspar. The albite, however, is almost invariably concentrated along potassium feldspar-oligoclase borders, rather than along potassium feldspar-quartz, etc., borders (fig. 1). The only



Fig. 3. Albite (ab) around inclusions of plagioclase in potassium feldspar. This type of albite is very rarely myrmekitic, as opposed to albite on the external borders of potassium feldspar. The sample is from the Doublehead pluton in the Front Range, Colorado. Crossed polarizers, X 75.

explanation for this concentration during exsolution is that the similarity of the lattices of albite and the more calcic plagioclase would result in a minimum interfacial free energy between the grains and thus a lower total free energy for the rock. This explanation assumes that such an extremely close approach to ultimate equilibrium (minimum free energy) exists in the granite that the free energy differences between albite-oligoclase and albite-quartz borders would be significant. It seems likely that granites do not approach ultimate equilibrium this closely, as shown by the presence of zoned plagioclase, albite, and oligoclase together, erratic distribution of deuteritic alteration products, and the simple fact that no granite consists merely of one giant grain of each mineral (which would yield the absolute minimum total surface area and the minimum interfacial free energy).

In some rocks fine-grained albite occurs along the borders between two adjacent potassium feldspar grains, but such occurrences are uncommon.

If the albite, therefore, has not been derived either from normal plagioclase grains or from potassium feldspar, it must have another source. The most likely source is a fluid, possibly the magma from which the remainder of the granite crystallized, or possibly a deuteritic or hydrothermal fluid permeating the solid rock. In order to determine the nature of this fluid, it is necessary to find the time of formation of the albite relative to the formation of the associated potassium feldspar.

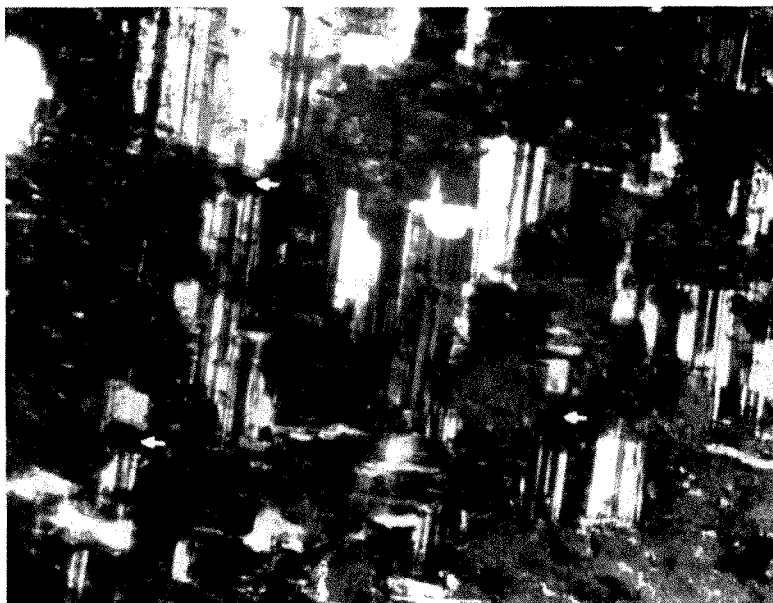


Fig. 4. Sodic plagioclase in oriented intergrowth in potassium feldspar (dark background). The discontinuity in albite (and other) twins between separate plagioclase grains indicates that this texture has not formed by replacement of plagioclase by potassium feldspar. Places where the discontinuity is particularly marked are shown by arrows. The sample is from the Conway granite of New Hampshire. Crossed polarizers, X 75.

TIME OF FORMATION OF ALBITE

Three possibilities exist for the time of formation of albite relative to the formation of associated potassium feldspar: (1) prior to the potassium feldspar; (2) after the potassium feldspar (presumably by replacement); and (3) synchronously. The first possibility, albite preceding potassium feldspar, is disproven by the geometrical arrangement of the two minerals; it is doubtful that the small albite grains would arrange themselves in some geometrical pattern which would later be filled in by a potassium feldspar grain.

The argument that the albite does not form after the potassium feldspar by replacement is based on the following facts. First, both the oriented albite rims on the normal plagioclase grains and the unoriented, fine-grained albite are generally restricted to portions of the potassium feldspar border adjacent to the oligoclase (fig. 2). If the unoriented albite grains had formed by replacement of the potassium feldspar, it seems likely that they would be randomly distributed around the potassium feldspar margins and that the adjacent plagioclase, quartz, or other grains would have no effect on the location of the albite. A second argument against a replacement origin for the albite is that albite very rarely, if ever, occurs in rocks in which the normal plagioclase is more calcic than about An_{25} or An_{30} , even if potassium feldspar is present. Deuteric activity is certainly not absent from comparatively basic rocks, and if albite is a deuteric replacement product, even fairly basic rocks should ex-

hibit some replacement of their potassium feldspar by sodic plagioclase (not necessarily pure albite).

If the albite, therefore, is neither pre- nor postpotassium feldspar, it is synchronous. In this connection it is interesting that the plagioclase equilibrium diagram (Bowen, 1913) shows that oligoclase of the general composition (An_{20-25}) found in granitic rocks should be in equilibrium with a melt of nearly pure albite. Thus, at the time of formation of potassium feldspar the Na/Ca ratio in the magma should be extremely high, and any plagioclase precipitated should be almost pure albite. The next section describes the plausibility that both albite and potassium feldspar crystallize together in the later stages of the solidification of granitic magmas and that this simultaneous crystallization yields the textures under discussion.

SIMULTANEOUS CRYSTALLIZATION OF ALBITE AND POTASSIUM FELDSPAR

The possibility of simultaneous crystallization of sodic plagioclase and potassium feldspar has been described in previous works. Sederholm (1928) found such a rapid and complex alternation of sodic plagioclase and potassium feldspar growth in some of the rapakivi granites of Finland as to indicate effective synchrony. A texture very similar to rapakivi has been described in the White Tank quartz monzonite (Rogers, 1958) and explained on the basis of simultaneous crystallization. In portions of the White Tank quartz monzonite, the potassium feldspar formed large crystals partly intergrown with, and mantled by, oriented sodic plagioclase; proof that the texture had not formed by replacement of plagioclase by potassium feldspar was shown by the fact that twin lamellae in plagioclase intergrowths were not continuous for distances over which they were continuous in the adjacent mantles, and this feature has been found in intergrown plagioclase and potassium feldspar in other granites (fig. 4). Additional evidence of simultaneous crystallization of the two alkali feldspars is found in adjacent large albite and microcline grains in pegmatites.

The examples cited above certainly do not refer to the fine-grained or rim albite discussed in the present paper. They are mentioned only to demonstrate that the concept of simultaneous growth of the two feldspars in granites is well established. The conclusion that the fine-grained and rim albite crystallized from a magma simultaneously with the potassium feldspar is based on the evidence in the preceding two sections, namely: (1) the albite formed from a fluid; and (2) the albite formed essentially synchronously with the potassium feldspar.

Previous work (Rogers and Bogy, 1958) has shown that a crystallizing potassium feldspar grain exerts a major influence on nucleation and growth of grains in its immediate neighborhood. For example, a growing potassium feldspar grain tends to prevent the formation of other potassium feldspar grains adjacent to it, possibly by causing abundant nucleation and incorporation of the nuclei in the already-growing grain. The effect of crystals during growth on their immediately adjacent environments is well established. Most hypotheses to explain crystal growth postulate the formation of a seedling of material in the fluid adjacent to the crystal, rapid attachment of this seedling

to the crystal surface, and spread of the seedling across the face. The seedling may be essentially "two-dimensional" or may have detectable three-dimensional thickness. Buckley (1951, p. 169-224) discusses various theories regarding the possibility of crystal growth by this type of promotion and incorporation of nuclei in the fluid adjacent to the crystal. The effectiveness of growing crystals in promoting nucleation around their margins is also demonstrated by the instantaneous "shower" of tiny crystals that results from dropping a seed into a supersaturated solution.

If, then, a growing potassium feldspar grain is an effective promoter for additional potassium feldspar nuclei, it may act in the same manner for other minerals with a similar lattice structure, such as albite. If crystallization occurs below the albite-potassium feldspar miscibility solvus, separate grains of albite should form adjacent to the potassium feldspar and may form inclusions. The restriction of the albite to the borders between potassium feldspar and normal plagioclase may indicate that the combined effects of nuclei promotion by both feldspars are necessary for the rapid precipitation of the small albite grains. Whatever the mechanism, it is apparent that equilibrium is not established between the albite and the adjacent more calcic plagioclase, even in those cases where rim albite forms by epitaxial orientation of the albite on the surface of the normal plagioclase grain.

The preceding discussion has not mentioned the formation of myrmekite, which is here considered to be a product of primary crystallization. Presumably, if quartz is crystallizing in the magma at the same time as the potassium feldspar and albite, the quartz and the feldspars may form intergrowths, especially where nucleation and growth are rapid. It is interesting that, although graphic intergrowths of quartz and microcline are widely considered to represent cotectic crystallization, the closely related myrmekite is generally considered to be a product of reaction in the solid state. There is no *a priori* reason, however, why the comparatively "regular" graphic texture should be more indicative of simultaneous crystallization than the "wormy" myrmekitic texture. Indeed, intergrowths between quartz and microcline are invariably regularly graphic regardless of whether they have formed by replacement or cotectic crystallization. Similarly, quartz-albite intergrowths are invariably wormy, and these facts suggest that the difference between the intergrowths is determined by the slight differences between the albite and microcline lattices and is not related to mode of formation.

Obviously not all of the albite and myrmekite in granitic rocks have the textural properties described here and on which the conclusion of primary precipitation has been based. To the extent that the textural features of the albite in any particular rock differ from these properties, then to that same extent its mode of formation may also differ from the origin proposed in this paper.

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NOTES ON FACETED SLOPES, ROCK FANS AND DOMES ON GRANITE IN THE EAST-CENTRAL SUDAN

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ABSTRACT. Although most of the residual hill masses in the east-central Sudan show fringing pediments separated by a sharp angular break from the hillslopes, many also show several additional small facets of slope parallel with the contours. When stripped of weathered debris, such faceted slopes reveal plane and convex sheets or lenses of granite separated by steeply dipping joints. Rock fans with sheeting parallel to their surfaces are recorded on both the fringing pediments and the lower hillslopes.

Mantled cone-shaped hills with straight side slopes appear to be modified to a dome form when stripped of their rock waste. Some domes retain concave and straight slope units on their sides whereas others become convexly faceted.

The production of faceted hillslopes, rock fans, and faceted domes on a homogeneous massive rock is believed to be due to unloading. Although if unloading occurs it will be a universal factor, its effect will be most clearly revealed when denudation is weak and slow in a stable area on hard elastic massive rocks.

INTRODUCTION

Steep isolated rocky hills surrounded by sandy fringing footslopes and set in a flat clay plain are characteristic of the savannah landscape around Qala en Nahl, Central Sudan (Ruxton, 1958). The surface sequence of solid rock, boulders, sand, and clay corresponds with the topographic sequence: buttress, hillslope, footslope, and plain. Rainfall in the area averages about 650 mm every year, falling mostly between May and September, and the mean annual temperature is about 28.5°C.

On most of the granite outcrops in this area partings are parallel with the ground surface. Gilbert (1904) noted partings with a curved surface "always adjusted to the general shape of the topography" and he thought these were due to "dilatation from unloading" (1904, p. 32). Watson (1910), Matthes (1930, 1936, 1950), Farmin (1937), Jahns (1943), White (1946), Waters (1952), and Chapman (1958) have all followed Gilbert in ascribing jointing, pseudo-bedding, and other partings related to the ground surface to unloading. The present paper attempts to show that in addition several minor landform features, including rock fans, on granite in the Sudan are most easily explained by this process.

Two granite batholiths occur in the area studied (fig. 1). In the Beila batholith various acid gneisses are intimately associated with granites and pegmatites. Large domes protrude up to 200 meters above the plain, some of them with well-developed rock fans. Fractures trending mainly NNW-SSE and NE-SW divide up the hill masses (fig. 2). The Ban-Balos batholith is of less massive biotite-microcline granite, and with one exception domes are only found on small satellite masses. Instead, rock ribs and buttresses are common. Some of the hills show a clear conical form with sheet structures visible under a thin cover of granite blocks.

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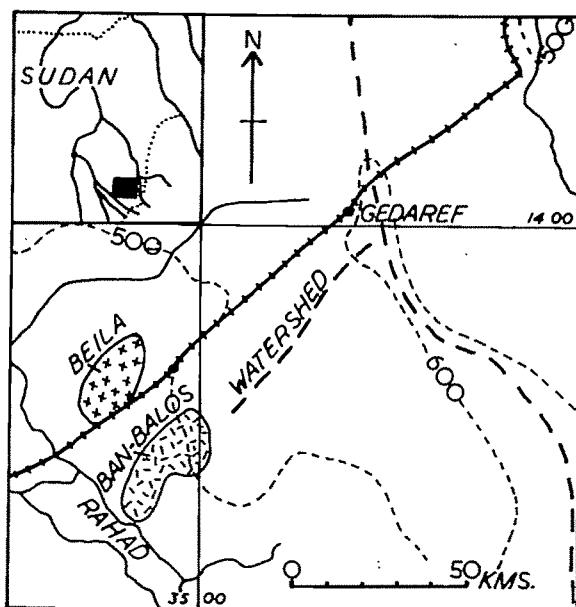


Fig. 1. Location map of the two granite batholiths.

The simplest slope profiles in both areas consist of four slope units separated by three inflexions or angles (fig. 3); the plain, plinth (footslope), hill-slope and hilltop are separated by the plinth angle, the piedmont angle, and a convex inflexion, respectively. Frequently there is a rock cliff between the mantled hillslope and the hilltop and it is marked by a buttress angle at its base (pl. 1, C). Nongenetic names are used instead of such terms as constant slope and pediment partly because of past confusion and also because on multi-faceted slopes each facet would need a separate name.

FACETED SLOPES, ROCK FANS AND DOMES

Faceted slopes.—Facets between the major angular breaks of the simple slope profile are most clearly developed on the hillslopes of the gneissose batholith. For example, on the southeastern side of Jebel Suleiman (fig. 4) a concave faceted slope is made up of seven straight or slightly convex units, each corresponding to an individual surface sheet of the granitic gneiss. Light and dark gray biotite-hornblende-gneiss are banded together with a general dip to the northeast of about 20° . They are intimately intruded with pink and gray massive biotite-granite, large banded pegmatites, and many quartz veins. The sheet joints crosscut all these rock types and appear to be completely independent of rock structure. Each sheet is between 1 and 3 meters in thickness and is terminated upslope and downslope by steeply dipping joints which in plan closely follow the contours (pl. 2, C; cf. Chapman, 1958).

On such faceted hillslopes there could be difficulty in deciding which angle is the piedmont angle. In this example it is clearly between the two facets with average slopes of 6° and 17° . The first convex facet above the piedmont

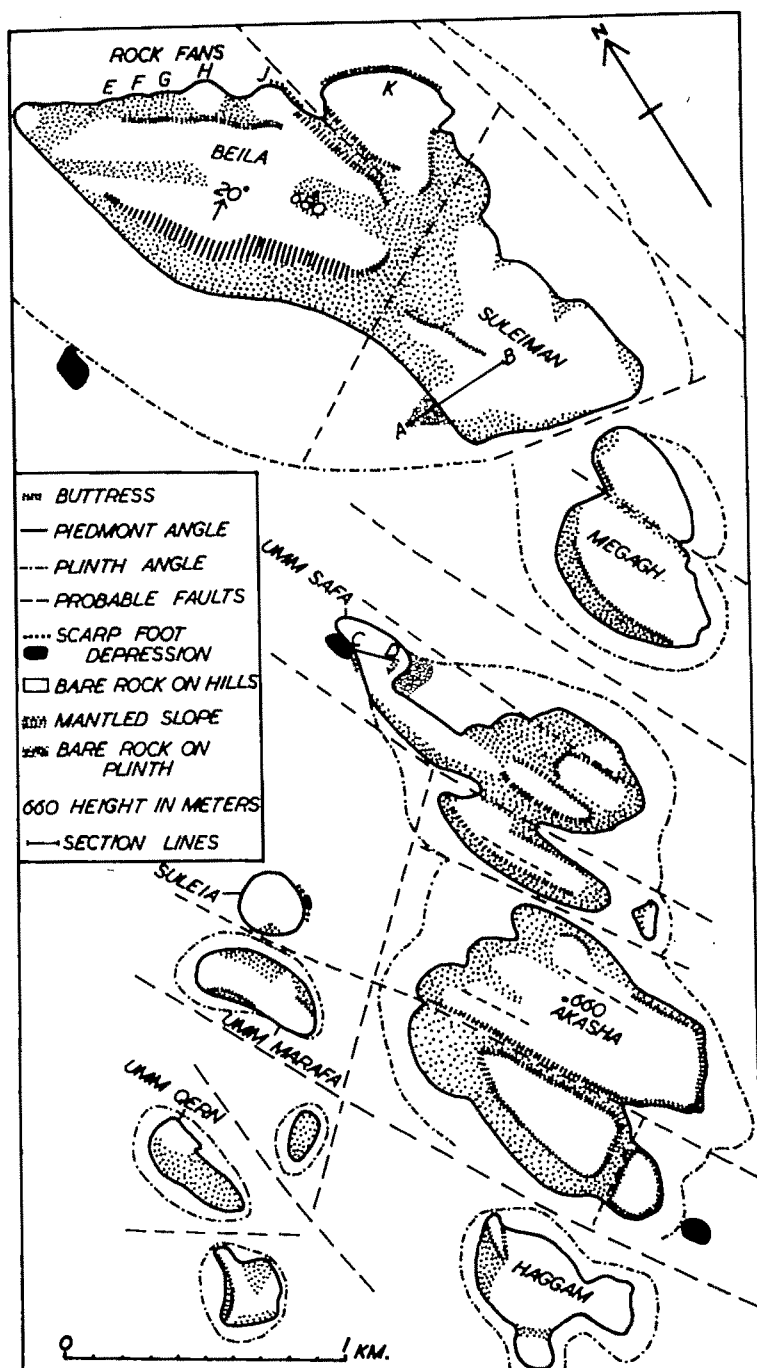


Fig. 2. Simplified geomorphic map of the Beila hill group.

angle might be interpreted as the subtalus buttress (Howard, 1942, p. 27). Such a convex surface could develop only if the talus were removed more slowly than it was formed (Fisher, 1866; Lawson, 1915); but there is no accumulation of talus at the piedmont angle. Talus is, however, found masking the buttress angle and sometimes at an angle between a rock cliff and the plinth.

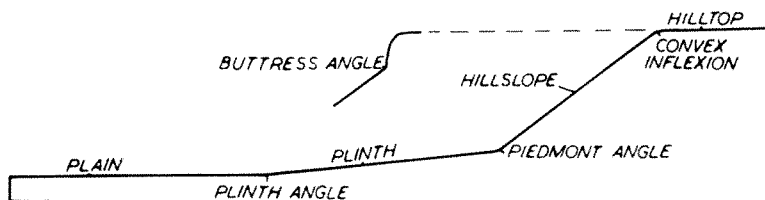


Fig. 3. The simple slope profile on granite and gneiss near Qala en Nahl.

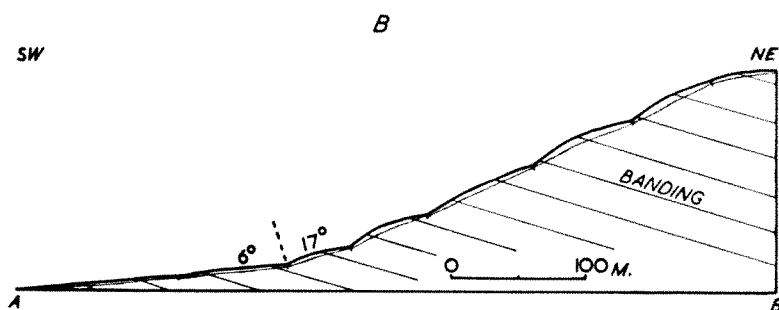


Fig. 4. A stripped faceted slope at Jebel Suleiman, natural scale.

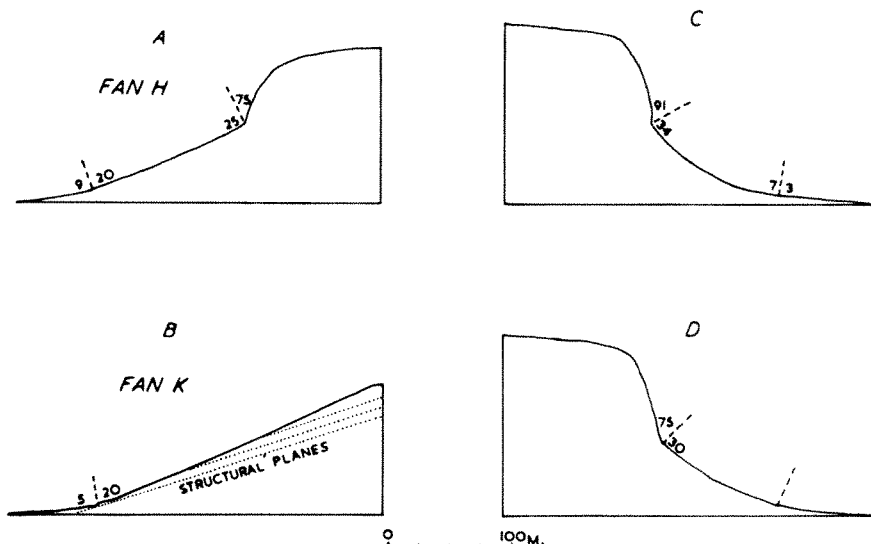


Fig. 5. Natural scale sections across Jebel Beila showing the rock fans to the northeast side (a) and (b), and the abrupt buttress angle on the southwest side (c) and (d).



Rock fans.—On the northeast side of Jebel Beila between the piedmont and buttress angles are six rock fans (fig. 2; pl. 1, A and B). Three are stripped bare (H, J, and K) and three are still largely covered with a thin sedentary and migratory layer of sand and boulders. In plan and section (figs. 2, 5A and 5B) these are of semiconical shape with slope angles between 20° and 26° , usually about 24° . They meet the plinth in an abrupt angle, and the fan "J" has a scarp foot depression some 5 meters deep at its base. This depression is a continuation of the N-S ravine cutting back into Jebel Beila, and so is merely a slight deflection of the normal drainage pattern.

To the east a very large rock fan "K" slopes at about 23° for a distance of 250 meters. This fan is more irregular than those to the west, and near its base the rock slope is 12° to 15° . Here it is markedly concave but in detail it is made up of straight sheet units. Neither the surface nor the sheeting parallel to it coincides with the structural banding or parting planes in the bedrock, and this is the more remarkable because the differences in dip are only a few degrees. A very long scarp foot depression, some 2 meters deep, at the base of this rock fan is not connected with any drainage feature on the hill mass.

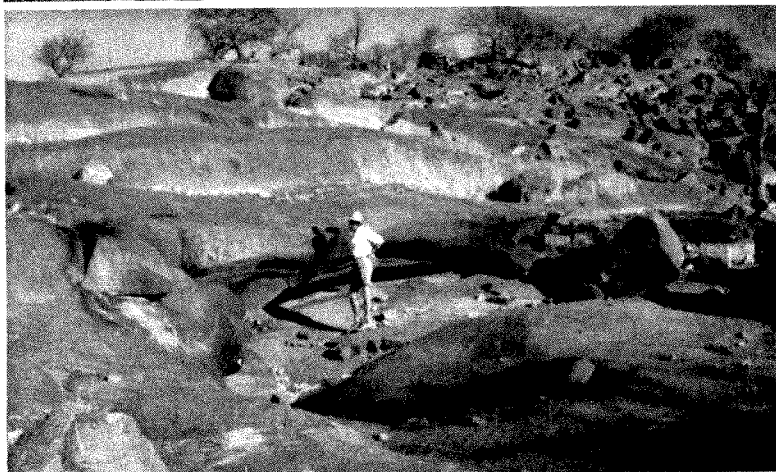
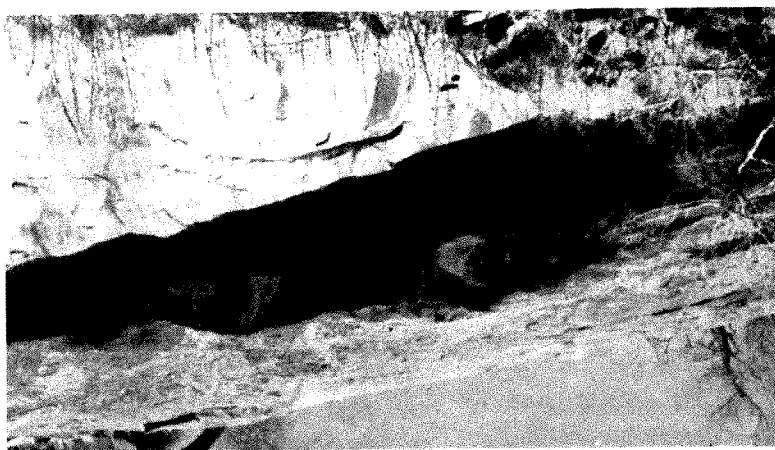
The steep southern face of Jebel Beila has a very sharp buttress angle between the bare rock (75° to 92°) and debris-covered hillslope (30° to 34°) mantled with boulders and chips of granite set in a gray-brown silty-sand matrix some 0.6 to 2 meters thick. This debris-covered slope is markedly concave, grading down to about 7° at the base where there is an abrupt change of slope to 3° or 4° on the upper plinth (fig. 5C and D). In plan the trace of the buttress angle is scalloped, with infacing V-shaped nicks where the debris-covered slope is higher and the rock cliff steeper (up to 92°) and outfacing convex curves where the debris-covered slope is lower and the rock cliff less steep (down to 75°). There is a suggestion both on the aerial photographs and on the ground that the infacing V-shaped nicks correspond to the apices of ill-defined rock fans.

Rock fans are also recorded between the plinth and piedmont angles at Jebel Qasim on the Ban-Balos batholith. Jebel Qasim stands on a very clear plinth (fig. 6) above the clay plain. On the western side the trace of the plinth angle has a V-shaped nick between two outfacing convex units. An incipient gully course heads ENE toward the upper plinth between these two units. Because the basal surface of continuously solid rock is about 3 meters' depth below the ground surface, complete stripping of this plinth would expose two rock fans.

Rock fans have seldom been figured or described, though many authors assume their existence (Rich, 1935). The rock fans claimed by Johnson (1932, p. 401) in the Sierrita Mountains, although confirmed by Davis (1938, p. 1385), were not found by Balchin and Pye (1956, p. 176). However, Mackin (1937, p. 883), Bradley (1940, p. 251), Hunt, Averitt, and Miller (1953), and Mabbutt (1955, p. 79) have noted rock fans in the Big Horn

PLATE 1

- A. Debris-mantled rock fan at the northeast side of Jebel Beila.
- B. Stripped rock fan on the northeast side of Jebel Beila.
- C. The buttress and piedmont angle on Jebel Beila.



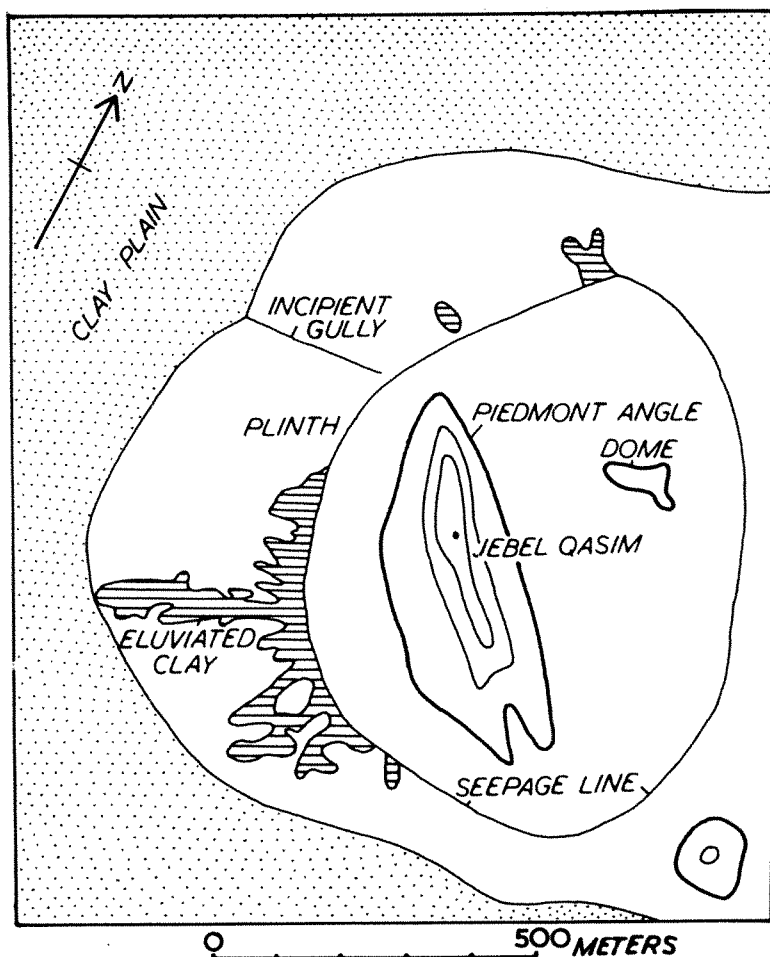


Fig. 6. Mantled rock fans on the plinth at Jebel Qasim.

Mountains, the Bridger Basin, Wyoming, the Henry Mountains, and in Little Namaqualand respectively.

It is usually assumed that rock fans are formed by laterally eroding streams or gullies issuing from a confined channel at the apex. Johnson (1932, p. 390) claimed that the existence of rock fans was critical evidence in the theory of pediment formation by lateral planation: pediments develop from rock fans. Hunt, Averitt, and Miller (1953, p. 190) describe the pediments around the Henry Mountains as a confluent series of rock fans formed by the action of rill wash or desert streams and not by lateral planation of the master

PLATE 2

- A. A large sheet cavern on Jebel Umm Qern.
- B. A large weather pit with greatest diameter coincident with sheeting, Jebel Qurein.
- C. Elongate tablets of granite derived from a sheet along the slope and contour joints, Jebel Qurein.

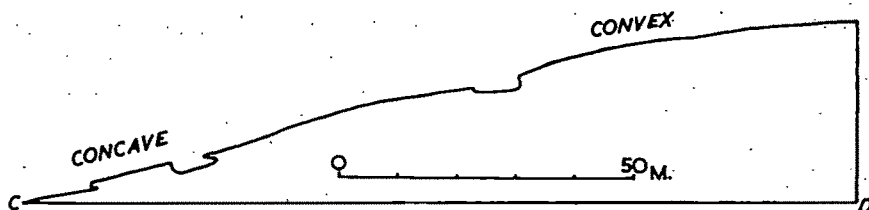


Fig. 7. The profile, to natural scale, of a granite dome at Jebel Umm Safa.

streams (mountain streams). Davis (1938) noted that Johnson's stripped rock fan in the Dragoon Mountains headed up into a pass from which no stream issued.

The rock fans in the Sudan do not appear to have been formed by the lateral cutting of either streams or gullies. There is no sign of concentrated water flow on them, neither is there a confined channel above the apex. Similar rock fans and faceted slopes have also been noted on granite in northern Ghana by one of the authors, and one of the rock fans in the Tong Hills is at the foot of a spur.

Domes.—Many nuclear hills still mantled with a layer of rock waste on the Ban-Balos batholith have a conoidal shape with an incipient dome form on their upper slopes, e.g. Jebel Ban. On stripping, the bare rock hills at first retain their simple slope profiles, e.g. Jebel Umm Safa (fig. 7), but later they appear to become modified in various ways. Large pits are weathered out at the intersection of steep joints and sheet joints (pl. 2, B), caverns are formed beneath some of the sheets (pl. 2, A), and depressions are excavated just below the piedmont or plinth angles.

There are not enough residual hills of similar size in any one small area to give a complete morphological picture of dome evolution. However, it appears that as a stripped residual hill gets smaller the dome form extends downwards, eliminating first the buttress angle and then the piedmont angle until a steep rock face meets the flat clay plain at an abrupt angle. If this change

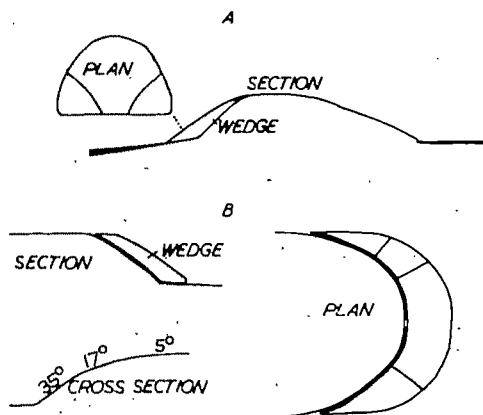


Fig. 8. Side-wedging of a granite dome near Jebel Qasim (a), and near Jebel Bia (b).

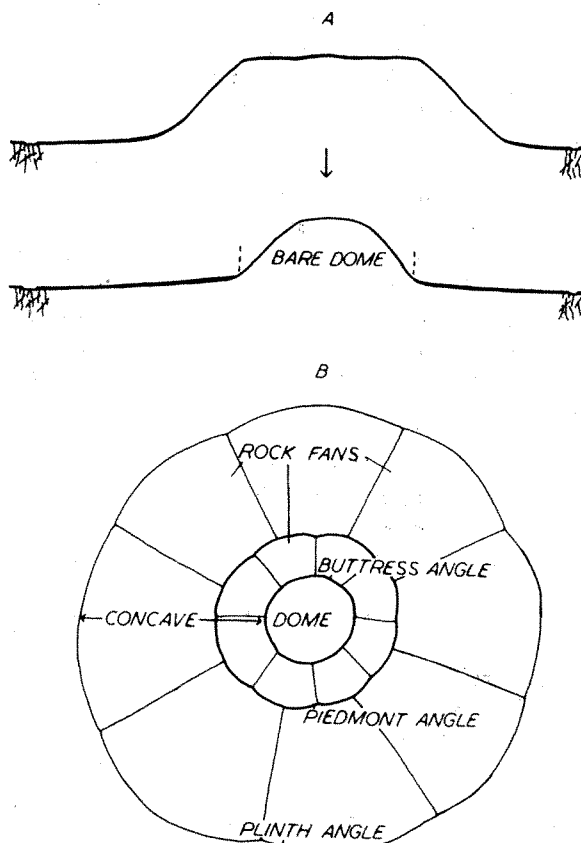


Fig. 9. Showing (a) the formation of a granite dome at the center of a topographic and structural compartment, and (b) the form in plan of the rock fans produced by unloading between the plinth angle and the buttress angle.

affects the whole hill, a perfect spherical dome results, e.g. Jebel Suleia. Usually, however, it affects only one side of the hill producing a half dome, e.g. Jebel Umm Safa and Jebel Umm Marafa. Many of these domes show deep channelling and fluting similar to that recorded by Branner in Brazil (1913, p. 173) and King in South Africa (1957, p. 89).

Several small elliptical domes (about 100 meters in length) occur around the larger hill masses on the Ban-Balos batholith. Most of them are flat domes which are being steepened by wedges of granite breaking off their sides (fig. 8A), but some higher domes are being flattened by concave-convex sheets breaking off their tops, e.g. Jebel Buweida. The lowering of larger domes by plating and the steepening of secondary domelets by marginal fracturing was also noted by Mabbutt (1952). One domelet near Jebel Bia has convexly faceted side slopes at 35° , 17° , and 5° (fig. 8B). The base of many of these satellite domes is undercut by caverns developed in the weathered rock. On the domelet near Jebel Qasim two sheets are developed on the north-eastern end. Whereas the upper sheet is broken up along regular joint frac-

tures, the lower, which is more weathered, is broken up along irregular polygonal fractures—"weathering fractures".

King (1953, p. 730; 1957, p. 86 and plates) claimed that parallel lateral slope retreat continues where a hill mass is bare or where it is mantled with a layer of rock waste. From evidence in the Central Sudan it seems that when the layer of moisture-retaining weathered debris is taken away the simple slope profile becomes considerably modified; chemical attack is much reduced and unloading assumes a greater relative importance. If the lower hillslope is stripped of debris a dome develops above the piedmont angle, and the buttress angle is eliminated. If the plinth is then stripped of its debris the dome may extend down to the flat clay plain, and a very sharp break of slope occurs.

Hillfoot depressions are a common feature of stripped hillslopes. They are linear depressions or circular hollows ("fulas"), which appear to be due to the removal of debris by wind eddies, animals, and mechanical eluviation, without renewal of supply from the bare hillslope.

Compartment evolution.—Most areas of massive granitic rocks are divided into compartments by shear zones and fault zones that are etched out by differential weathering and erosion. Relief of load on denudation may then be both upward and outward against the weakened denuded frameworks, giving a tendency for convex sheeting to develop. However, water erosion in a savannah climate tends to develop a concave profile toward the depressed frameworks. In combination both processes produce concave faceted profiles. Moisture concentration and, therefore, chemical weathering are accentuated at the thin marginal parts of the sheets, particularly where these are intersected by steep vertical joints. There is thus a tendency for sapping to occur at the foot of each slope facet. The greatest contrasts in chemical weathering are between bare rock, seasonally moist debris, and perennially moist debris, and these three occur in order on the rock cliff, the lower mantled hillslope, and the upper footslope, and so the buttress angle and the piedmont angle are accentuated. The plinth angle, when present, is formed by the lateral cutting of water courses, usually small gullies.

In the later stages of compartment evolution a very clear division can be drawn between three main areas of denudation. Unloading and mass-wasting are dominant in the central domelike portion, weathering and erosion are dominant between the buttress and plinth angle, and water transport is dominant on the clay plain. Unloading of the central core tends to produce a dome form (fig. 9A), but unloading of the concentric strips of the lower mantled hillslopes and the plinth tends to produce rock fans (fig. 9B).

Near Qala en Nahl domes, rock fans, and faceted slopes are best developed on the massive gneiss and less well developed on the granite. A few domes have also been recorded on solvsbergite, trachyte, serpentine, and even one on talc-magnesite.

DISCUSSION

Sheeting broadly controls topography when denudation is relatively slow and long continued but is reorientated when strongly concentrated erosion by water or ice creates relatively rapid topographic changes (Jahns, 1943, p. 81). Chapman (1958) and Chapman and Rioux (1958), from a study of massive

granite in Maine, found a close interdependence of jointing and topography, contour and slope joints being preferentially developed across the sheets. This interdependence is also clear in the way in which adjacent monoliths have independent joint systems. In an arid region it may be that, once a piedmont profile is developed with plinth, piedmont and buttress angles unloading parallel to each slope unit may assist in a continuation of parallel slope retreat (Ruxton, 1958, p. 377).

In arid and semiarid regions the upper surface of continuously solid rock (the basal surface, Ruxton and Berry, 1960) and the effective depth of water penetration on granitic rocks is often limited to the depth of unloading. Removal of soil and upper weathering zones leads to a renewal of the weathering profile by the release of a sheet or sheetlike layer of jointed rock. If this sheet is thin (less than 1 meter), a mass of gravelly residual debris is usually formed from it (Zone IIIa, Berry and Ruxton, 1959, p. 59). If it is thicker, corestones and residual debris (Zones II or III, Ruxton and Berry, 1957) usually develop first. If the sheeting takes place on a bare rock surface, only the base of the sheet is vigorously attacked by chemical weathering, and sheet caverns may result. In each case renewal takes place in steps, each step being due to the release of a sheet unit.

If there is a long interval between the release of each sheet, as on a foot-slope, then microcycles of weathering and erosion will occur in step with the unloading. In the Qala en Nahl region such microcycles of sheet release, weathering, eluviation, compaction, and gullying probably cause the regrading of the upper plinth.

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DRAINAGE ALIGNMENT IN WESTERN SOUTH DAKOTA*

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ABSTRACT. Northwest-southeast stream alignment in western South Dakota coincides with the prevailing wind direction. This alignment appears to be due to the periodic accumulation of locally derived eolian sediments in drains which are not aligned. Because of this deposition, unaligned drains are not elongated by water erosion as rapidly as those which are aligned. Eolian sediment can be derived locally and deposited when the prairie vegetation is destroyed by fire or weakened by drought.

INTRODUCTION

The northwest-southeast alignment of the tributary streams of the east-flowing rivers of western South Dakota and of streams in other plains states has been attributed to wind action. The prevailing winds are from the northwest. Although Russell (1929, p. 255) considered other modes in the area where Pierre shale is the upper formation, he suggested the alignment probably was induced by sand dunes in an earlier period. Baker (1948, p. 8) proposed that the drainage pattern was caused by the integration of deflation basins. Later, Flint (1955, p. 159) discussed the dune and deflation hypothesis and concluded:

"Although some form of eolian control seems the probable explanation of the lineated topography, the exact mechanism of stream development is not yet clear."

Soil studies in the area where Pierre shale is the main soil parent material have helped to establish the mechanism.

DISCUSSION OF THE DUNE HYPOTHESIS

As pointed out by Flint (1955, p. 159), "... longitudinal dunes are not present in most of western South Dakota in which the parallel drainage pattern occurs." Thus, the alignment would have to be relict from the time the dunes migrated across the area. Any drainage entrenchment would follow the ancestral aligned channel. However, the short, geologically young tributaries of the White and Bad Rivers tend to be aligned. Their alignment cannot be attributed to some historic event. Crandell (1958, p. 50) concluded the drainage alignment was formed from middle Pleistocene time to the present.

DISCUSSION OF THE DEFLATION HYPOTHESIS

Deflation basins formed in weathered shale are numerous in broad upland areas between the eastflowing rivers in western South Dakota. According to Baker (1948, p. 7), wind erosion may have been more active during the glacial epochs. Some of the basins may have been initiated at the same time as some of the frost features found in the soils of the area. Baker (1948, p. 8) suggests the basins may be enlarged by the eolian removal of material that is powdered and flocculated by desiccation following ponding. If rain were sufficient to cause ponding, vegetation should be abundant at the edge of the basin by the time it became dry. This vegetation should collect any aggregates of clay

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moved by saltation so that a dune would form. None have been found either at the southeast edge of the few basins examined in the field or reported in the literature about this area. It is doubtful that much sediment could be removed from the basins by winds without a dune's forming unless the vegetative cover was absent. Crandell (1958, p. 49) observed a dense growth of vegetation in basins which were swamps or ponds earlier in the season.

Contrary to the idea of "... deposition by winds in ridges with depression scouring . . ." (Baker, 1948, p. 8), the soils usually are thinner on the narrow ridges than in the adjacent upland valleys or basins. The reverse should be true if deposition occurred on the ridges. In addition, no olive-colored eolian mantle of Pierre sediments has been found on soils formed from Tertiary bedrock that occur south of Pierre-derived soils. If large quantities of clay sediment had been removed from the soils, parna should have been deposited as in Australia (Butler and Hutton, 1956).

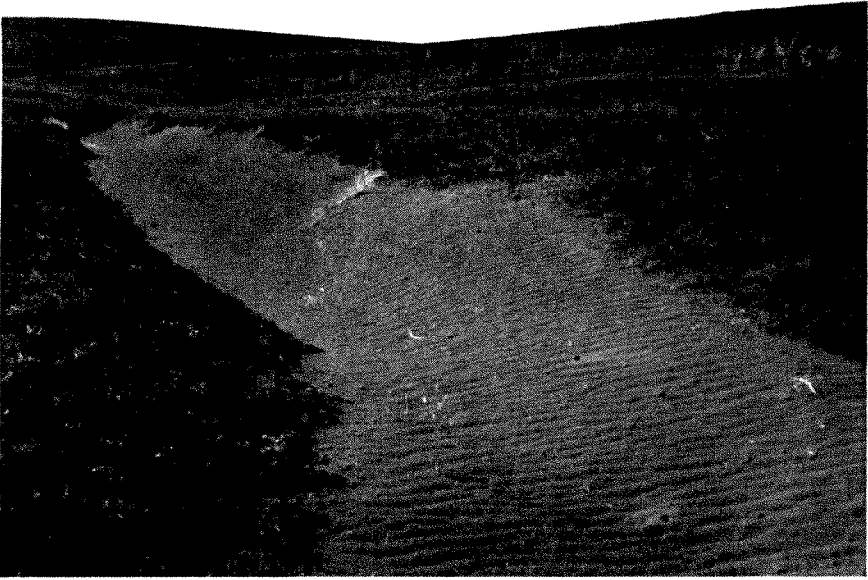
The quantity of material removed by deflation cannot be estimated at this time. Fine sediment should be available for deflation because soft aggregates of clay would be abraded if moved for great distances by saltation. Clay dunes may not form because of this abrasion.

PROPOSED MECHANISM FOR STREAM ALIGNMENT

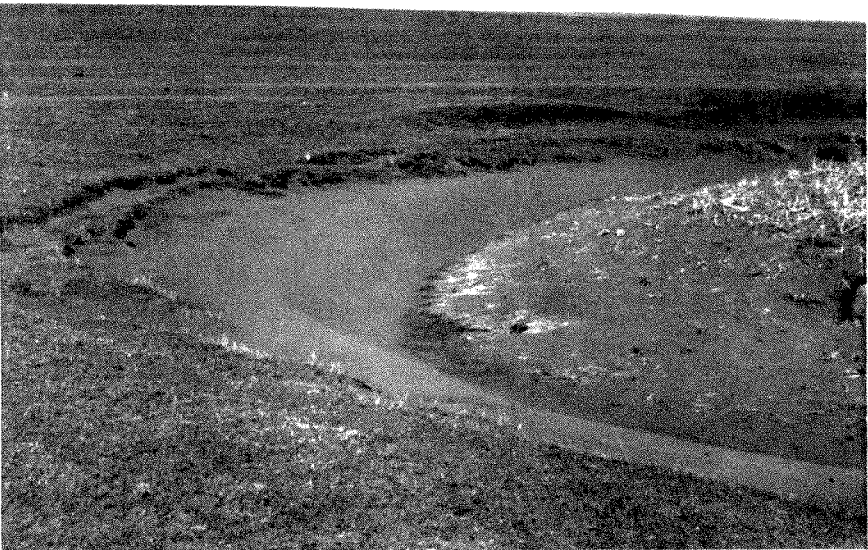
Wind erosion is restricted to periods when prairie vegetation is not abundant enough to protect the soil surface. This could occur during prolonged droughts or following prairie fires. Two areas where the vegetation had been destroyed by prairie fires were examined in the spring of 1959. The first area (northwest part T. 5 N., R. 24 E., Haakon County) had the vegetation burned in the fall of 1958. The soil surface was unprotected except for the short, partly burned crowns of the grasses. The soil surface of the second prairie fire area (northwest of Vivian, South Dakota) was similar to that in the first. The fire near Vivian was on April 6, 1959, when northwest winds attained velocities up to 65 miles per hour.

Wind-transported aggregates of clay were deposited in both fire areas. The eolian deposits range from a fraction of an inch to about three feet thick. No accumulation of eolian sediment was found on the ridge tops or on smooth slopes. Most of it occurred in drainageways which were oriented in some direction other than northwest-southeast (pl. 1A). Those drains oriented northwest-southeast did not accumulate any eolian material except where there was either a shallow entrenched channel meander which curved away from this direction or where a short, shallow gully had formed in the otherwise channel-free drain. In these meanders or short gullies eolian material had accumulated below the bank along the northwest side of the channel. The eolian material was mainly clay in the upper part, but a mixture of clay and partially burned grass segments were in the lower part. This filling of meanders which were not oriented northwest-southeast also occurred along a small, intermittent, aligned stream (Sec. 33, T. 107 N., R. 79 W., Lyman County) which had a gently sloping valley more than a half mile wide (pl. 1B). At several sites, where a small drain without a distinct channel branched headward into two smaller drains, the one of these in the aligned direction received no sediment, whereas the

PLATE 1



A



B

Wind-transported aggregates of clay have accumulated in a shallow gully of an east-west-oriented drain (A) and in the northwest part of a meander in a northwest-southeast-oriented, intermittent stream (B).

other accumulated a thin mantle. Later in the season, western wheatgrass had grown through the thin mantle to help stabilize it against erosion. Before the area was settled and grazed heavily, many of these drains probably supported tall-grasses (prairie cordgrass, switchgrass and big bluestem) with fibrous root systems capable of stabilizing an eolian mantle in a short time.

The destruction of the protective prairie cover by fire was more widespread before the area was settled. Many prairie fires caused by lightning are extinguished by man each year. From personal observations in a three-year period, much of the lightning occurs with local thundershowers which do not yield enough precipitation to moisten the grass thoroughly. Fires started during these showers would burn large tracts of prairie before they would be extinguished by natural processes. The prairie usually is dry and will burn readily in the late summer or autumn and early spring. Prior to settlement, fire probably destroyed the prairie cover of an area every few years. Then the unprotected soil surface could be eroded by winds.

It is postulated that the stream alignment is caused by the deposition of locally derived eolian silt and sand-size aggregates of clay in drainageways. Small drains oriented northwest-southeast at the heads of streams would not accumulate the mantle, so that water erosion could progress more rapidly in them than in the unoriented drains which collected the eolian sediment. Any deviation away from the direction of the prevailing winds by the small creeks would be counteracted by the accumulation of eolian material in this segment of the channel. Larger streams and rivers would not be affected by the small quantity of eolian material deposited in their channels.

This mechanism for stream orientation allows water to erode most of the sediment from the area by the downcutting of the oriented drains and by slope retreat. Winds would transport small amounts of sediment and deposit most of it locally in certain landscape positions. The unequal deposition of these eolian sediments would control the direction and rate of elongation of small drains.

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THE PROBLEM OF REBEDDED POLLEN IN LATE-GLACIAL SEDIMENTS AT TAUNTON, MASSACHUSETTS

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ABSTRACT. The occurrence of pollen of tree genera not found in the modern flora of the United States and Canada in late-glacial sediments from the Williams Street bog near Taunton, Massachusetts, is considered evidence of contamination of the sediments with secondary pollen rebedded from pre-Quaternary deposits. Nearby varved clays also contain these pollen types, and because the local till contains little if any pollen, it is concluded that the secondary pollen was carried in glacial meltwater from the vicinity of Tertiary deposits 25 miles to the northeast. The late-glacial bog sediments were apparently contaminated either directly by meltwater streams, or through the erosion and redeposition of meltwater stream deposits. As the secondary pollen spectrum cannot be determined with certainty, it is impossible to interpret the mixed secondary and primary pollen spectrum contained in the late-glacial sediments.

INTRODUCTION

American pollen analysts have recently become concerned with a serious source of error in pollen analysis, the contamination of deposits with pollen from older sediments. Pollen grains are sometimes able to undergo more than one cycle of deposition without perceptible change in morphology; thus a single stratum may contain morphologically similar pollen grains derived from plants widely separated in time. Unless the rebedded or "secondary" pollen is distinguished from "primary" pollen derived from vegetation living at the time the sediments were deposited, its occurrence in sediments may lead the pollen analyst to erroneous interpretations of vegetational history.

The presence of rebedded pollen in late-glacial deposits in Denmark was demonstrated by Iversen (1936). He found that boulder-clay and varved clay in the vicinity of contaminated deposits contained pollen and other microfossils from Tertiary sediments that had been over-ridden and eroded by the ice sheet. The late-glacial minerogenic sediments were contaminated with a similar assemblage of pollen but contained in addition pollen derived from the late-glacial vegetation. Iversen showed that, if the spectrum of secondary pollen was determined from samples of nearby boulder-clay or varved clay, it could be subtracted mathematically from late-glacial pollen spectra. Vegetational history could then be studied as it was recorded by the primary pollen.

Secondary microfossils in glacial drift have also been reported in this country. Mather, Goldthwait, and Thiesmeyer (1942) and Sayles and Knox (1943) concluded that microfossils in tills and glacial silty clays on Cape Cod, 25-50 miles east-southeast of Taunton, were derived from interstadial or interglacial marine deposits that had been over-ridden and eroded by glacial ice.

Recently most pollen investigators working with inorganic late- and postglacial sediments in America have considered the possibility that the sediments were contaminated with rebedded pollen. In most cases the criterion for suspecting contamination was the occurrence, in the same strata, of pollen grains from genera and species that are apparently ecologically incompatible

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in the present vegetation. In two instances (Andersen, 1954; Martin, 1958) pollen types which conflicted with vegetational and climatic interpretations based on the majority of the pollen in clays and sandy sediments, and which were therefore considered secondary, were subtracted from the pollen sum, and "corrected" pollen diagrams were published. In other cases (Leopold, 1956; Livingstone and Livingstone, 1958; Davis, 1958; Ogden, 1959), pollen types for which a secondary origin was suspected were plotted on the diagrams but given less weight in the vegetational and climatic interpretation than other pollen types. In no instance, however, was the investigator able to demonstrate the source of the putative rebedded pollen, or to employ the objective subtraction method of Iversen (1936).

In the course of analyzing the pollen in a core from a bog near Taunton, Massachusetts, the author found evidence of contamination of the late-glacial sediments with pollen rebedded from pre-Quaternary deposits. This paper reports this evidence and presents the results of an investigation of the possible sources for rebedded pollen at Taunton. The problems of estimating the extent of contamination and of interpreting pollen analyses of contaminated sediments are discussed.

ACKNOWLEDGMENTS

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EVIDENCE OF REBEDDED POLLEN

The pollen diagram from the Williams Street bog near Taunton, Massachusetts (Davis, 1960) is similar in its major features to pollen diagrams from other parts of southern New England (Leopold, 1955; Leopold and Scott, 1958; Davis, 1958). It appears to record the development of forest during the Two Creeks interstadial (pollen zones T and A-1.2-3), the decline in frequency of pine and deciduous trees relative to spruce during the Valders stadial (zone A-4), and the subsequent decline of spruce and increase in the frequency of pine and deciduous trees (zone B). (The upper levels of the deposit, in which deciduous tree pollen is presumably abundant, were not analyzed because of poor pollen preservation.) The stratigraphy of the core is as follows:

- 0-2.77 m Brown peat with wood and moss fragments. Loss on ignition 98-99% dry weight (2 samples). Pollen zone C (presumably).
- 2.77-2.86 m Coarse fibrous peat with grasslike leaf fragments. Loss on ignition 97% (1 sample). Zone B-2.
- 2.86-3.43 m Very fine fibrous peat. Loss on ignition 52-83% (2 samples). Zone B-2.
- 3.43-3.62 m Very fine fibrous peat grading to gyttja. Loss on ignition 30% (1 sample). Zone B-1.

- 3.62-4.00 m Gray-green gyttja. Loss on ignition 19-22% (5 samples). Zone A-4.
- 4.00-4.41 m Green-brown gyttja. Loss on ignition 22-29% (5 samples). Zone A-1-2-3.
- 4.41-4.47 m Fibrous peat with grass-like leaf fragments. Loss on ignition 25% (1 sample). Zone A-1-2-3.
- 4.47-4.95 m Gray silty sand streaked with dark gray sand. Sand at 4.80 m. Loss on ignition 2-4% (6 samples). Zone T?.
- 4.95-5.20 m Medium coarse sand. Loss on ignition 1-2% (5 samples). Zone T?. It was not possible to penetrate deeper with the Hiller borer.

A major difference between this diagram and others in southern New England is the occurrence, in the lower levels of the deposit, of pollen of genera that are not found in the modern flora of the United States. Pollen of *Platycarya*, a genus now limited to Asia, was found at 4.52, 4.85, 4.95, 5.05 (2 grains), 5.15 (7 grains), and 5.20 m (8 grains); *Pterocarya*, also limited to Asia, at 5.10 m (1 grain); and *Engelhardtia-Aljaroa*, limited to Asia and Central America, and to Central America, respectively, at 4.80, 5.05 (3 grains), 5.15 (2 grains) and 5.20 m (8 grains). *Platycarya*, *Pterocarya*, and *Engelhardtia* have all been reported from Tertiary deposits in this country, and *Pterocarya* has also been reported from the Pleistocene of Maryland (LaMotte, 1952; Leopold and Scott, ms.). As these genera do not occur in the modern flora, and are not recorded in the postglacial fossil record, it seems improbable that they grew in the vicinity of Taunton at the time of the retreat of the ice. A far more plausible explanation is that their pollen has been rebedded from Tertiary deposits. If this is so, Tertiary pollen types that are indistinguishable from the pollen of modern species may also be rebedded in the sediments in which these pollen types occur. The presence of primary pollen as well is implied by the general similarity of the pollen spectra at these levels to pollen zone T at other sites.

To subtract secondary pollen from a mixed spectrum of primary and secondary pollen, it is necessary to know the complete spectrum either of the primary pollen or of the secondary pollen. As the purpose of the original investigation was to discover the primary pollen spectrum, no assumptions as to its nature are justified. It may be possible, however, to determine the secondary pollen spectrum from older pollen-bearing sediments in the vicinity, or from till or glacial clay deposited by a glacier that had eroded such sediments. Because the secondary pollen may have been derived from several different deposits, analyses of older sediments in the vicinity may not include all the secondary pollen types, nor represent them in the proper proportions. In any event, older pollen-bearing sediments (other than varved clay) are not known in the Taunton quadrangle (Emerson, 1917). Difficulties may also be encountered in attempts to recover the secondary pollen spectrum from glacial deposits. Iversen (1936) found identical pollen spectra in till and glacial clay in Denmark and concluded that all the pollen in both types of deposit was secondary. This implies that plants did not live within pollen dispersal distance when the ice was active and when the varved clay was deposited. It cannot be

assumed that this was true in Massachusetts, as late-glacial pollen diagrams record a comparatively rapid immigration of trees onto the newly deglaciated landscape. Thus supraglacial till and glacial clay in this region may contain primary as well as secondary pollen.¹

In an attempt to determine the spectrum of secondary pollen rebedded in the Williams Street bog sediments, samples of nearby ground moraine, flowtill and varved clay were analyzed for their pollen content.

POLLEN ANALYSIS OF TILL

Four samples of unweathered till were collected from borrow pits and building excavations in the vicinity of the Williams Street bog. The locations of the collections are shown in figure 1. Samples A and B are flowtill, ablation moraine which slid as a mudflow from the surface of glacial ice onto stratified sand and gravel (Hartshorn, 1958). Samples C and D are ground moraine and contain abundant stones of the local bedrock.²

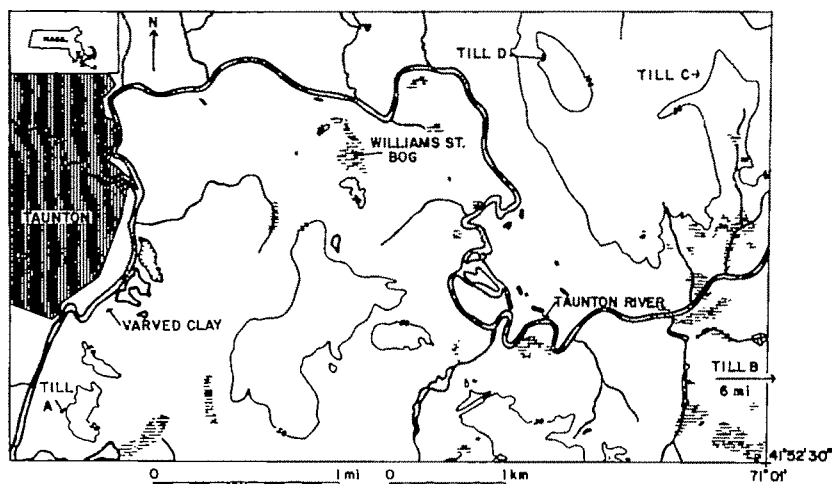


Fig. 1. Outline map of a portion of the Taunton quadrangle, showing locations at which samples were collected. Contour interval 50 ft, datum mean sealevel. Inset shows approximate location in state of Massachusetts. Drawn from U. S. Geological Survey topographic map, 1:24000, revised 1949.

The samples were treated in the laboratory with HF and HCl, as recommended by Heinonen (1957). Bromoform flotation (Frey, 1951) was also used as a final step to remove the precipitate which formed in hydrofluoric acid. No pollen grains were found in samples B and D, although 1 grain (*Fraxinus*-type) was found in an empty tube put through the extraction procedure as a control for contamination at the same time that sample B was prepared. Three grains were found in sample C: 1 *Fraxinus*-type, 1 *Ambrosia*, and 1 *Pinus*. Unfortunately no control was run on the day this sample was

¹ The occurrence of leaf and seed fossils of arctic-alpine plants in varved clay in the Connecticut Valley, Massachusetts (Emerson, 1898) further indicates that varved clay may contain primary pollen.

² I am grateful to J. P. Schafer for sending me till samples B, C and D.

prepared, but the occurrence of pollen in a previous control suggests that the sample was originally devoid of pollen. By contrast, Heinonen (1957), using much the same laboratory method and the same size samples, was able to extract from 0.9,340 tree pollen, 0.3,340 herb pollen, and 0.980 spores from samples of basal till from Finland. A few pollen and spores were extracted from sample A by means of repeated bromoform flotation of fines washed from a 600 gm sample. Heinonen (1957) has shown that this method is much less effective than HF for extraction of pollen from till, because most of the pollen occurs in a crust of fine particles adhering to the larger stones. A further disadvantage to the method is the increased possibility of contamination, as large amounts of reagents are used and the large sample is exposed to air for the several hours required for the procedure. Fifteen pollen and spores were found in sample A: 3 *Ambrosia*, 3 *Betula*, 1 Compositae, 1 *Fraxinus*, 1 *Pinus*, 1 unknown, 1 *Lycopodium*, and 4 fern spores. Unfortunately no control was run at the time the sample was prepared, but when a control was put through the same procedure some months later, 6 pollen grains were found. It seems likely that most of the pollen grains and spores found in this sample also represent laboratory contamination.

Even if it is assumed that the till samples contain pollen in addition to laboratory contamination, the numbers of grains are so low that it seems unlikely that either the till or the glacial ice from which it originated could have served as a principal source of secondary pollen. In any event, pollen of *Platycarya*, *Pterocarya*, and *Engelhardtia-Alfaroa* would be unexpected in the till, because the nearest known Tertiary sediments from which the pollen might have been derived are located approximately 25 miles to the northeast (Emerson, 1917). Tertiary pollen would occur in the ground moraine at Taunton only if ice had eroded these sediments and subsequently flowed 25 miles to the southwest. The general direction of glacial flow was apparently not toward Taunton, however, but to the southeast (Flint and others, 1959).

POLLEN ANALYSIS OF VARVED CLAY

In contrast to the till, varved clay from the Taunton quadrangle contains abundant pollen. Samples were collected from the south wall of a claypit just east of the Taunton River (fig. 1). Sample E was collected about 8 ft below the surface of the clay, 3 ft below an unconformity between gray varved clay and overlying brown oxidized clay, sample F from a thick varve 1 ft lower in the section, and sample G about 50 ft further west, 2 ft below a thick varve believed to be the same as that from which sample F was collected. Pollen was extracted without difficulty by flotation in bromoform, boiling in 10% KOH, and acetolysis, and was stained and mounted in glycerin. About 350 pollen and spores were counted from each sample. It is assumed that laboratory contamination was not significant; if any occurred it would represent only a small proportion of the abundant pollen extracted from each sample.

Over fifty different pollen types were found in the varved clay. The percentages are shown in table 1. (For comparison, the table also shows the pollen spectrum from 5.20 m depth in the bog sediments.) The percentages of pollen in the three clay samples appear similar, but not identical. Differences in per-

TABLE 1

Pollen percentages in varved clay samples, and sample from 5.20 m level
at Williams Street bog

Pollen or spore type	Percentage in sample			
	E	Varved clay F	G	Bog sediment 5.20 m
<i>Abies</i>	1.9	0.3	0.3	0.1
<i>Acer saccharum</i> -type	—	0.3	—	—
<i>Alnus</i>	4.0	1.4	2.6	4.7
<i>Ambrosia</i> -type	—	—	0.3	0.4
Anacardiaceae	0.5	—	0.5	0.6
<i>Artemisia</i> -type	0.5	1.4	0.5	0.8
<i>Betula</i>	11.7	23.1	27.6	6.1
<i>Carya</i>	5.3	2.2	1.8	—
Caryophyllaceae	—	—	—	0.7
<i>Castanea</i>	3.5	—	2.9	2.0
<i>Cephalanthus</i> -type	1.3	0.6	0.5	0.3
Chenopodiaceae	—	—	0.5	0.1
<i>Corylus</i>	4.0	1.7	2.9	1.5
Cupressineae	2.4	1.4	0.5	0.2
Cyperaceae	0.5	2.8	0.5	19.7
<i>Engelhardtia</i>	1.3	—	—	1.0
Ericaceae	—	1.1	0.5	2.0
<i>Fagus</i>	—	0.3	0.5	—
<i>Fraxinus</i>	2.7	1.7	1.3	1.3
Gramineae	2.9	2.5	1.8	6.9
<i>Ilex</i>	0.3	0.3	0.3	—
Leguminosae?	—	0.3	0.3	—
<i>Liquidambar</i>	—	0.3	—	—
<i>Myrica</i>	0.3	0.6	0.3	0.8
<i>Nymphaea</i>	0.3	—	—	—
<i>Nyssa</i>	3.5	5.0	4.2	0.8
<i>Ostrya-Carpinus</i>	1.1	0.3	0.5	0.3
<i>Picea</i>	0.5	1.9	1.0	3.8
<i>Pinus</i>	8.5	8.1	12.2	29.2
<i>Plantago</i>	—	—	—	0.1
<i>Platycarya</i>	2.4	0.3	0.3	0.9
<i>Platycarya</i> or <i>Engelhardtia</i>	0.5	—	—	—
<i>Pterocarya</i>	0.3	—	—	—
<i>Populus</i>	0.5	0.8	1.0	—
<i>Potentilla</i>	—	—	—	0.1
<i>Quercus</i>	6.6	12.5	16.7	1.8
Rosaceae	—	0.3	0.3	0.1
<i>Rumex</i>	—	—	—	0.1
<i>Sagittaria</i> -type	0.3	—	—	—
<i>Salix</i>	—	2.5	0.8	3.9
<i>Symplocos</i>	—	0.6	0.8	—
<i>Thalictrum</i>	—	—	—	0.9
<i>Tsuga</i>	0.3	0.6	0.3	—
Tubuliflorae	1.3	—	1.8	1.2
Typhaceae	—	0.6	0.3	—
<i>Ulmus</i>	—	—	—	0.2
Umbelliferae	—	0.6	1.0	0.3
<i>Viburnum</i>	0.3	—	—	—
Vitaceae	2.4	3.3	—	0.3
Unknown pollen	20.2	9.7	8.4	3.7
Unknown, type I	0.5	0.6	—	0.1
Filices	3.7	6.7	2.6	1.0
<i>Isaetes</i>	—	0.3	—	—
<i>Lycopodium</i>	—	0.3	—	0.1

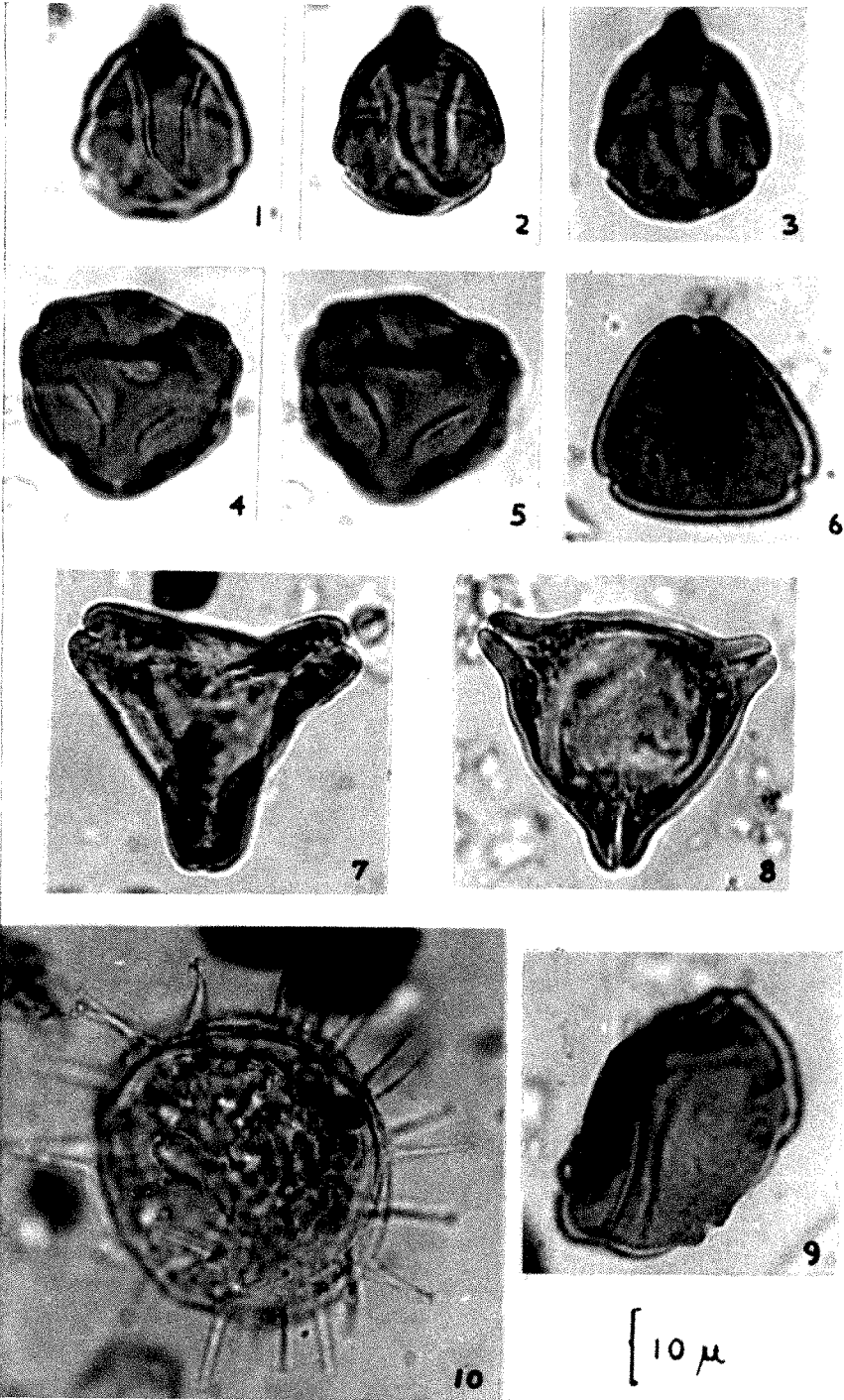
TABLE 1 (Continued)

Pollen or spore type	Percentage in sample			
	E	Varved clay F	G	Bog Sediment 5.20 m
<i>L. selago-lucidulum</i>	—	—	—	0.2
<i>Sphagnum</i>	1.6	3.3	1.3	1.1
Unknown spores	1.3	0.6	—	0.1
"Hystrix"	0.5	—	—	—
	100%	100%	100%	100%
Number pollen and spores counted	376	353	384	894

centages may be due to mistakes in identification, as well as to statistical error, as many of the pollen types found were unfamiliar to the author. Lower percentages of *Betula* and *Quercus* in sample E, however, may represent a real difference between this sample and the others.

Of particular interest is the occurrence in the varved clay of *Platycarya*, *Pterocarya* and *Engelhardtia-Alfaroa* pollen. Photomicrographs of these types are shown in plate 1, figs. 1-6, 9. Many of the pollen types in the clay are unlike those I have seen in Quaternary deposits in Massachusetts and are only tentatively identified or are listed as "unknown". Many of these unknown types were also observed in the bog sediments. For example, "Unknown, type I" (pl. 1, fig. 7) was found at 4.85, 4.90, 5.05 (2 grains), 5.10 (4 grains), 5.15 (2 grains), and 5.20 m. This pollen is characterized by very heavy exine thickenings around the pores (colpae?) and appears similar to a pollen type found in upper Cretaceous and Eocene deposits and, as rebbed pollen, in postglacial marine clays in Sweden (Fries and Ross, 1950: cf. pl. 1, fig. 7). A similar pollen type, "Unknown, type II" (pl. 1, fig. 8), appears identical to pollen known from upper Cretaceous and Paleocene sediments in Germany, and, as a rebbed fossil, in late- and postglacial marine clays in Sweden (Fries and Ross, 1950: cf. pl. 1, fig. 6). Several types of spherical microfossils with forked spines were found; one of these "Hystrix" types is shown in plate 1, figure 10. Similar microfossils are known from Cretaceous and Tertiary marine sediments in Europe, and have been reported in Quaternary tills and clays, where they apparently have been secondarily deposited (Iversen, 1936; Fries and Ross, 1950). "Hystrix" is thought to be a marine protozoan, but its exact affinities are unknown. It represents an extant form, as appears to be indicated by its occurrence in postglacial freshwater peat, near a contact with salt-marsh peat, at the John Hancock fishweir site at Boston, Massachusetts (Wilson, 1949).

Apparently some, and perhaps all, of the pollen in the varved clay has been rebbed from older deposits. As the ice in the immediate vicinity seems to have contained little if any pollen, the secondary pollen must have been carried from some distance, presumably by glacial meltwater. This conclusion is supported by studies of the stones in outwash deposits at Taunton, which indicate meltwater transport from the northeast (J. H. Hartshorn, personal communication). In addition to pollen derived from Tertiary (and Creta-



ceous?) sediments, the meltwater may have transported pollen derived from interglacial and interstadial deposits that were eroded by the ice, and pollen from vegetation then growing some distance from Taunton. It is also possible that the varved clay contains primary pollen from plants growing within pollen dispersal distance of Taunton at the time the varved clays were deposited.

A previous investigation of the varved clays at Taunton (Hyyppä, 1955) led to quite different conclusions. Hyyppä identified pollen of twelve native tree genera in the varved clay. He assumed all the pollen was primary and considered the predominance of deciduous tree pollen evidence of deposition during an interstadial when a "southern deciduous climate" prevailed not far outside the margin of the glacier ice. On the basis of the occurrence of marine, brackish water and a few freshwater diatom species in the varved clay he concluded that the clay was deposited in a shallow marginal sea. However, I consider the presence of pollen of exotic genera, even though it occurs in low percentages, evidence that the clay is contaminated with rebedded microfossils. For this reason the microfossils are unreliable as vegetational and climatic indicators of the conditions that prevailed at the time the clay was deposited.

DISCUSSION

The sediments in the Williams Street bog apparently were contaminated with secondary pollen either through the erosion and redeposition of varved clay, or through the direct action of meltwater streams flowing into or over the site of deposition. The first of these hypotheses seems unlikely because the surface of the varved clay is at least 10 to 20 ft lower than the esker and kame or lake deposits that surround the bog. However, it is conceivable that other outwash deposits (e.g. the kame deposits?) were eroded and redeposited as the ice block underlying the site of deposition melted. If these outwash deposits contained pollen from meltwater streams deposited contemporaneously with the pollen in the varved clay, the spectrum found in the varved clay would be similar to the spectrum of pollen deposited secondarily in the bog sediments. Even when these assumptions are made, however, it is still not possible to ap-

PLATE 1

Microfossils from varved clay sample E. The photomicrographs were all made with an oil immersion lens, and have been equally enlarged. Scale indicated in lower right-hand corner of plate.

Figs. 1-3, *Platycarya*. Fig. 1, focus on upper surface of grain, Fig. 2, focus on optical cross section of pores, Fig. 3, focus on lower surface of grain.

Figs. 4-5, *Platycarya*-type ? Fig. 4, focus on optical cross section of pores, Fig. 5, focus on lower surface of grain.

Fig. 6, *Engelhardtia-Alfaroa* ?, focus on wall, and optical cross section of pore in upper portion of photograph. This grain resembles cf. *Engelhardtia* pollen from the late-Tertiary of Denmark (Ingwersen, 1958). Other grains seen resembled modern pollen more closely.

Fig. 7, "Unknown, type I", focus on surface of wall in upper left-hand portion of grain, showing pore (colpus?), and on optical cross section of upper right-hand pore, showing heavy exine thickenings.

Fig. 8, "Unknown, type II", focus on optical cross section of colpae, showing heavy exine thickenings.

Fig. 9, *Pterocarya*, focus on uppermost, folded portion of grain. Only one of the five pores is clearly in focus.

Fig. 10, "Hystrix", focus on two of the many forked spines. Other "Hystrix" types seen were larger, with heavier spines.

ply Iversen's (1936) subtraction method. Iversen divided the secondary pollen spectrum into two groups: Group A included pollen of extinct Tertiary genera, and Group B included pollen which could not be distinguished from Quaternary pollen types. He demonstrated that the ratios of pollen types within Group A remained constant in late-glacial sediments, regardless of the total amount of Group A pollen present. Assuming, therefore, that the ratio of Group B pollen to Group A pollen had also remained constant, he subtracted pollen types belonging to Group B in the ratio to Group A in which they had occurred in the till. Group A pollen was also subtracted, and the remaining pollen was assumed to be of primary origin. This method cannot be used here because the pollen of exotic genera (Group A) occurs in low frequencies both at the bog and in the varved clay deposit; the ratio of Group B to Group A pollen cannot be calculated with statistical accuracy.

The sediments may also have been contaminated by a meltwater stream flowing over the site before the underlying ice had melted, or into the site after melting had begun. In this case the spectrum of pollen in the varved clay is not necessarily the same as the secondary pollen spectrum in the bog sediments, as the varved clay may contain both primary pollen, and secondary pollen brought in by other meltwater streams. Assuming the bog sediments were contaminated directly by glacial meltwater, they may be of the same age or only slightly younger than the uppermost levels of the varved clay deposit. If samples had been collected higher in the clay section, it might have been possible, by comparing the pollen spectra with those found in the lowest levels of the bog deposit, to test this hypothesis.

Direct contamination by glacial meltwater is in contrast to the mode of contamination described in Europe. In Denmark and Finland the boulder-clay is often rich in pollen (Iversen, 1936; Heinonen, 1957). Pollen and fine inorganic debris were apparently washed from the moraines and redeposited in lakes and ponds during periods of intense solifluction. Autochthonous, organic late-glacial sediments, deposited when slope-wash was not effective, are often entirely free of secondary pollen; usually the amount of contamination varies with the clay content of the sediments (Iversen, 1936, 1947; Krog, 1954). At Taunton, however, the erosion and redeposition of till and outwash deposited by local ice would not have resulted in extensive deposition of secondary pollen. If the deposition of secondary pollen depended upon meltwater streams, there is no necessary correlation between the amount deposited and the loss on ignition of the sediments, nor between the amount deposited and the severity of the climate.

As the spectrum of secondary pollen deposited in the bog sediments has not been determined with certainty, the spectrum of primary pollen remains unknown. Mixed primary and secondary pollen spectra are meaningless—they represent vegetation that never existed at a point in time, and vegetational interpretations cannot be attempted. Above the 4.52-m level, however, pollen of *Platycarya*, *Pterocarya*, *Engelhardtia-Alfaroa* and "Unknown, type I" were not found. The sediments above 4.52 m may be free, or nearly free, of contamination, and a vegetational interpretation based on the major constituents can be made with reasonable confidence.

CONCLUSIONS

The problems of identifying secondary pollen and estimating the extent of contamination are obviously difficult even when a considerable amount of data is at hand. Subtraction of secondary pollen is possible only when the complete spectrum is known from the source materials, and when the recognizable secondary types (such as exotic genera) occur in frequencies sufficient to permit subtraction by Iversen's (1936) method with statistical accuracy. Supposed ecological incompatibility of plants represented in the pollen spectrum is not a sufficient criterion for the recognition of secondary pollen, because: (1) the latter may include a variety of pollen types from deposits of different ages, (2) it may not represent a community distinguishable from late-glacial vegetation (Donner, 1957), and (3) the late-glacial vegetation itself may have been made up of species which do not occur together today (Drury, 1956; Benninghoff, 1957). Even if two distinct communities are recognized within the pollen spectrum, choice of one of them as primary and the other as secondary involves a preconception on the part of the investigator. Where there is evidence of contamination, but no way of estimating its nature or extent, pollen investigators might better abandon attempts at interpretation than run the risk of reaching erroneous conclusions.

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GRAPTOLITE FAUNA OF THE POULTNEY SLATE

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ABSTRACT. The graptolite faunas of the Poultney slate are Early and Middle Ordovician in age. Four zonal assemblages are recognized in the formation as well as elements of others. The zonal sequence is identical to that in the lower part of the Ordovician succession in the Marathon region, Texas, and it indicates that deposition was continuous in the northern part of the Taconic area for all of the early part of the Ordovician. This is the first record of the earliest Ordovician graptolite zones in the eastern part of the United States.

INTRODUCTION

During the reinvestigation of the well-known, graptolite-bearing Schaghticoke, Deepkill, and Normanskill black shales in the region near Albany, New York, structural and faunal as well as spacial breaks between the units became readily discernible. A question posed by the breaks was: were they the result of regional unconformity formed during the time represented by them, or were they the result of structural deformation? To answer this question, attention was turned to the northern part of the Taconic area, to Washington County, New York and the adjacent part of Vermont. Here a formation named the Poultney slate by Keith (1932, p. 403) was said to be "Lower Ordovician as indicated by the graptolites." Keith further stated: "Graptolites were first found by Walcott in his early work on the Cambrian and have since been found by many geologists." He indicated that the Poultney slate was underlain by the Lower Cambrian, Hooker slate and that it was overlain conformably by the Indian River slate. Also, he said (p. 404) that Ruedemann had assigned the graptolites in the Poultney and Indian River slates to the "Normanskill horizon of the Albany area." This statement contradicts that on the previous page that the age of the Poultney slate was Early Ordovician, because at that time the Normanskill shale was considered to be Chazy or Early Middle Ordovician in age. Thus Keith himself created confusion over the age of the Poultney slate.

Despite Keith's mention of numerous graptolite collections, no faunal lists from the Poultney slate have ever been published. Further, the unit has not been mentioned in the literature nor mapped since Keith's work until recently, when Shumaker and Theokritoff have mapped it in the Granville, Pawlet, and Thorn Hill quadrangles.

LITHOLOGY AND FAUNA

The Poultney slate consists of black shale with some interbedded layers of blue-gray-weathering, black limestone which are commonly one to two inches thick in the lower part and interbedded black and green argillite which appears waxy in the upper part. The upper part of the formation weathers to a characteristic chalk white. Lenses and beds of brown-weathering quartzose sandstone are interbedded with the other lithologies in places. They are more common in the lower part of the formation than in the upper part of it. Also, in a few places, red argillite is interbedded with the green and black argillites in the upper part of the unit.

The Poultney slate is underlain conformably by a unit composed of rusty-weathering, sooty, black shale and interbedded rusty-weathering, tan, quartzose sandstone which bears graptolites considered Latest Cambrian by the writer. The Poultney slate grades upward into the red and green slates which comprise the Indian River slate. Graptolites identical with those from the Normanskill shale have been collected from lenses of black slate in this formation.

The writer examined many exposures of the Poultney slate, several with Theokritoff, and was able to re-collect from a fossil locality originally found by Theokritoff as well as from new ones. Although graptolite fragments are plentiful within the black layers of the formation, complete specimens are difficult to find. All but one of the collections made by the writer came from the lower part of the formation. The one exception was collected from the highest beds.

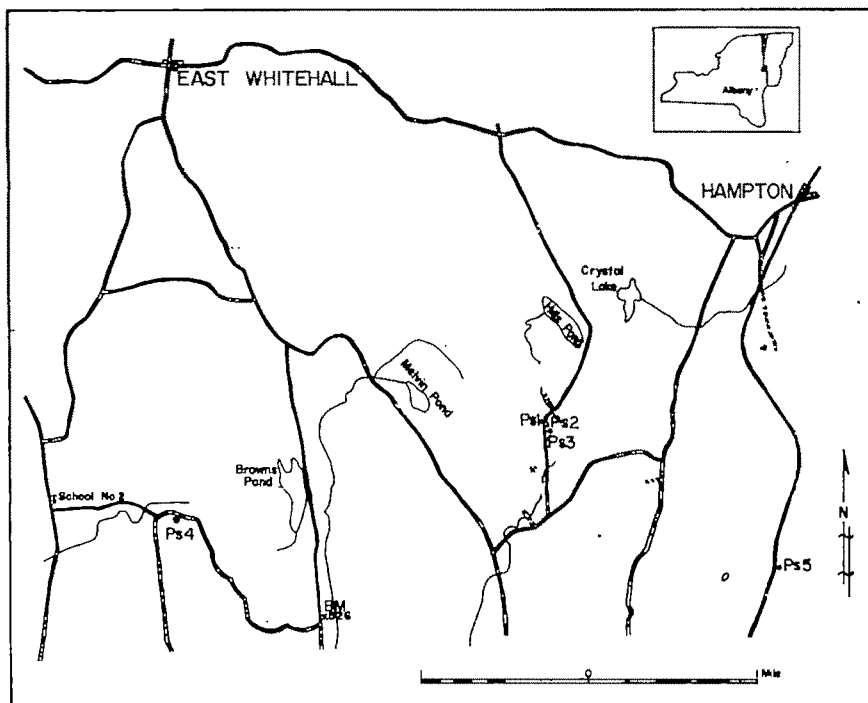


Fig. 1. Map of area near Hampton, New York showing localities where good collections were obtained.

The location of the places from which good collections were obtained is shown on the map (fig. 1). Collections Ps-1, 2, and 3 are from a short but continuous stratigraphic section in the lower part of the formation, possibly about 100 to 300 feet above the base. Collection Ps-4 is from 50 feet, stratigraphically, above the base, and collection Ps-5 is from the highest beds of the unit—in an interval where the Poultney slate grades into the Indian River slate. The faunal lists for each collection are given below.

- Ps-1. From 2 miles S49W from Hampton, New York
Adelograptus aff. *A. pauxillus* (Benson and Keble)
Adelograptus sp.
Clonograptus flexilis (Hall)
Dichograptus cf. *D. maccoyi* Harris and Thomas
Dichograptus sp.
Didymograptus extensus (Hall)
Didymograptus nitidus (Hall) ?
Didymograptus sp.
Tetragraptus approximatus (Nicholson)
- Ps-2. From 20 feet above Ps-1
Dichograptus octobrachiatus (Hall)
Didymograptus ensj ensis Monsen
Didymograptus sp.
- Ps-3. From 65 feet above Ps-2
Adelograptus sp.
Clonograptus cf. *C. milesi* (Hall)
Dichograptus octobrachiatus (Hall)
Didymograptus extensus (Hall)
Didymograptus cf. *D. patulus* (Hall)
Didymograptus aff. *D. validus* Tornquist
Tetragraptus fruticosus (Hall) (4-branched form)
Tetragraptus quadribrachiatus (Hall)
Tetragraptus sp.
- Ps-4. From 4.15 miles S63W of Hampton, New York
Adelograptus aff. *A. divergens* (Elles and Wood)
Adelograptus cf. *A. pauxillus* (Benson and Keble)
Adelograptus simplex (Tornquist)
Adelograptus sp.
Clonograptus aff. *C. timidus* Harris and Thomas
Clonograptus sp.
Didymograptus ? sp.
- Ps-5. From 2.15 miles S3W of Hampton, New York
Amplexograptus aff. *A. perexcavatus* (Lapworth)
Climacograptus phyllophorus Gurley
Climacograptus sp.
Cryptograptus tricornis (Carruthers)
Dicellograptus divaricatus var. *salopiensis* Elles and Wood
Glyptograptus euglyphus var. *pygmaeus* (Ruedemann)
Leptograptus sp.

The assemblage of forms in each collection is closely similar to those which characterize the lower zones of the Ordovician graptolite zonal sequence delimited by the writer (1960) in the Marathon region, Texas. The assemblage of collection Ps-1 is typical of zone 3, that of collections Ps-2 and Ps-3 is characteristic of zone 4, and that of collection Ps-4 is nearly identical to that of zone 2. Collection Ps-5 probably can be referred to the zone of *Nemagraptus gracilis* (zone 11) but it may represent the zone of *Climacograptus bicornis* (zone 12). Not enough distinctive elements are in it to be certain.

TABLE 1

Correlation of graptolite-bearing units in the Taconic area

	GRAPTOLITE ZONES	CLASSIC UNITS	NORTHERN TACONICS
UPPER ORDOVICIAN	15 <i>Dicellograptus complanatus</i>		
	14 <i>Orthograptus quadrimucronatus</i>		
MIDDLE ORDOVICIAN	13 <i>Orthograptus truncatus</i> var. <i>intermedius</i>	Snake Hill shale	Indian River slate
	12 <i>Climacograptus bicornis</i>	Normanskill shale	
	11 <i>Nemagraptus gracilis</i>		Pouliney slate
	10 <i>Glyptograptus teretiusculus</i>		
	9 <i>Halograptus etheridgei</i>	Deepkill shale	
	8 <i>Isograptus</i>		
	7 <i>Didymograptus bifidus</i>		
	6 <i>Didymograptus protobifidus</i>	Deepkill shale	
	5 <i>Tetragraptus fruticosus</i> 3 and 4 br.		
LOWER ORDOVICIAN	4 <i>Tetragraptus fruticosus</i> 4 br.		
	3 <i>Tetragraptus approximatus</i>		
	2 <i>Clonograptus</i>		
	1 <i>Anisograptus</i>	Schaghticoke shale	

In addition to these collections, one from the basal beds of the formation exposed on the top of Mount Rascal in the Hartford, New York quadrangle, 18.75 miles S22W of Hampton, New York includes specimens of *Clonograptus* cf. *C. tenellus* (Linnarsson). This form is a characteristic element of the fauna of zone 1 in the Marathon region and it is common in the Early Tremadoc rocks in Europe.

The writer examined collections at the U. S. National Museum made by Walcott and Prindle from the slate belt in Washington County, New York in the latter part of the 1880's. The location of these old collections is noted on Dale's (1899, pl. XIII) map of the area. Two of the collections can, from the writer's observations of the stratigraphy and Zen's (1959, pl. A-2) map, be accurately located stratigraphically. They are both from the middle part of the Poultney slate. One is from 0.8 miles north of North Granville, New York and 6 miles S47W of Hampton, New York. The species *Didymograptus protobifidus* Elles was obtained here. This dependent form characteristically occurs in the zone bearing its name in the Marathon zonal sequence and is common in the middle part of the Deepkill shale. The second collection is from 3 miles north Fairhaven, Vermont and 7.7 miles N10W of Hampton, New York. The one species in this collection is *Tetragraptus fruticosus* (Hall).

CORRELATION AND CONCLUSIONS

The correlation of the Poultney slate with the Marathon region graptolite zones is shown on the correlation chart (table 1). The probable correlation with the Schaghticoke and Deepkill shales is also indicated.

The Poultney slate is Early and early Middle Ordovician in age. It includes rocks that are the probable correlatives of the Schaghticoke and Deepkill shales. Also, it includes rocks which do not have any fossiliferous correlatives in the Albany, New York area. Diagnostic graptolite zonal assemblages that will permit sure correlation with the Deepkill shale have not as yet been found in the Poultney slate. However, the presence of *Didymograptus protobifidus* and many fragments in the middle and upper parts of the formation indicate a probable correlation with part of the Deepkill shale and that younger assemblages may be found with more searching. The lower part of the formation has yielded graptolites diagnostic of zones 1 through 4; the highest beds bear a zone 11 or 12 assemblage. Although no definitive faunal evidence of continuous deposition is present in the intervening strata, no unconformity is present in the interval. Therefore, the writer suggests that the formation represents a record of continuous deposition from the Earliest Ordovician into the Middle Ordovician. The break or gap between the Schaghticoke and Deepkill shales and that within the Deepkill shale (Berry, 1959) probably has a structural explanation.

Thus the graptolite fauna of the Poultney slate has yielded an important clue to the depositional history of the Taconic area. Also, the zonal assemblages constitute the second recorded occurrence of Early Ordovician graptolite zones in eastern North America and the first in the eastern United States.

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OCCURRENCE OF SILICIFIED WOOD IN HAWAII*

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Silicified wood has been found at two localities on the Island of Hawaii. Samples have been collected from the littoral cone, Puu o mahana, about 2.5 miles northeast of Kalae, the southernmost point of the Island, and from a bed of ash on the southwest slope of Mauna Kea, 0.5 mile north of Kilohana Girl Scout Camp on the Saddle Road. The writers have not personally visited the second locality but have received samples and information about the occurrence from Glenn G. Mitchell of Hilo.

Puu o mahana is a littoral cone built by the explosions generated when a prehistoric lava flow from Mauna Loa reached the sea. It consists of alternating beds of fine-grained basaltic ash and relatively coarse lithic debris with an abundance of olivine crystals scattered throughout. Unconformably overlying the vitric-lithic beds of the cone are a series of partially indurated and highly altered (palagonitized) beds of very fine-grained ash up to 20 feet thick. This material is generally believed to represent reworked Pahala ash, which originally was produced by Kilauea Volcano, 40 miles northeast, during a prehistoric era of strong phreato-magmatic activity. The cone is being eroded by waves, and a green sand (olivine) beach of striking appearance has formed on the adjacent shore.

On Puu o mahana the silicified wood occurs plentifully in the uppermost 10 feet of the cone; none has been observed in the overlying weathered Pahala ash. In the locale studied, the wood appears as vertical tubelike concretions, many of which branch downward and presumably represent the roots of some plant that grew on the surface of the cone prior to or contemporaneous with the deposition of the Pahala ash. The upper parts of the plant probably were carried away by the wind or decayed before the process of silicification began.

Thin sections of the Puu o mahana wood show poor preservation of the cellular structure, suggestive also of some decay prior to silicification. However, enough tissue is preserved to leave no doubt as to the original vegetable nature of the petrifications. The wood ranges from about $\frac{1}{4}$ inch to $2\frac{1}{2}$ inches in diameter, and pieces up to 2 feet in length have been recovered. Almost every piece has a crusty layer of ash adhering to it and the colors of the core run from tan to dark brown with an intermingling of cream. Chemically, the material proves to be opal, consisting of 93.88% SiO_2 , 4.15% H_2O^+ , 0.64% H_2O^- , and 1.33% remainder.

Volcanic ash, because of its fine grain and commonly glassy nature, weathers rapidly and releases soluble silica (Murata, 1940). Plant materials, therefore, when embedded in ash, have a much better chance of becoming

* Publication authorized by the Director, U. S. Geological Survey.

silicified before they disappear through complete decay, than in any other matrix. In the case of the Hawaiian petrified wood, the silica was very likely derived from the overlying highly weathered Pahala ash. Silica, soluble in the ground water, percolated downward through the littoral cone, and was re-deposited as opal in the woody root remains and other open channelways. Although the common association of silicified wood with siliceous volcanic ash is well known, the Hawaiian material is of special interest because it indicates that a much less siliceous tholeiitic basalt ash also serves as a source of readily available silica.

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DISCUSSION

THE EFFECT OF SEDIMENT TYPE ON THE SHAPE
AND STRATIFICATION OF SOME
MODERN FLUVIAL DEPOSITS

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In a recent paper, Schumm (1960) proposed the hypothesis that the weighted mean percent of silt and clay contained in the channel and bank deposits of valleys in semiarid regions is of primary importance in determining the width-depth ratio of these channels. To illustrate this relation, Schumm presented a graph (fig. 1, p. 179) showing the regression of channel width-depth ratio ($W/D = F$) against the weighted mean percent silt and clay (M); the graph shows a high degree of negative correlation between the two variables ($r = -.91$), indicating, hypothetically, that relatively broad, shallow channels are associated with channel and bank deposits with low silt and clay content, and relatively narrow, deep channels are associated with channel and bank deposits with high silt and clay content. This appealing hypothesis, unfortunately, is not supported by the material Schumm presents. The reason is simple: the variable M , weighted mean percent silt and clay, as defined by Schumm, contains the variable F or W/D , width-depth ratio, in disguised form.

Schumm defined the variable M as follows:

$$M = \frac{Wm_1 + 2Dm_2}{W + 2D}, \quad (1)$$

where W is channel width, D is channel depth, m_1 is the percent of silt and clay in the channel deposit, and m_2 is the percent of silt and clay in the bank deposit (1960, p. 178). If the percentages of silt and clay in the channel deposit and bank deposit are identical, then $m_1 = m_2 = M$. If m_1 and m_2 differ, as is most commonly the case in ephemeral streams, M will contain information about the channel shape.

In plotting values of F against M , Schumm was essentially saying that

$$F = W/D = f \left(\frac{Wm_1 + 2Dm_2}{W + 2D} \right); \quad (2)$$

$f()$ stands for some functional relationship. If we assume, for simplicity, that $m_1 = 0$, $m_2 = 50\%$, and insert these values into equation 2, we find that

$$W/D = f \left(\frac{100D}{W + 2D} \right), \quad (2a)$$

that is, $M_{0.50} = 100D/(W + 2D)$. It is easily seen that W/D and $M_{0.50}$ are mathematically dependent. For every value of W/D there is a unique value of $M_{0.50}$. The relation between the two variables is inverse, as can be seen by reference to figure 1. One can select other values for m_1 and m_2 , and as long

as $m_1 < m_2$, the relation between W/D and M will similarly be inverse. For example, if $m_1 = 5\%$, $m_2 = 75\%$, then

$$W/D = f\left(\frac{5W + 150D}{W + 2D}\right). \quad (2b)$$

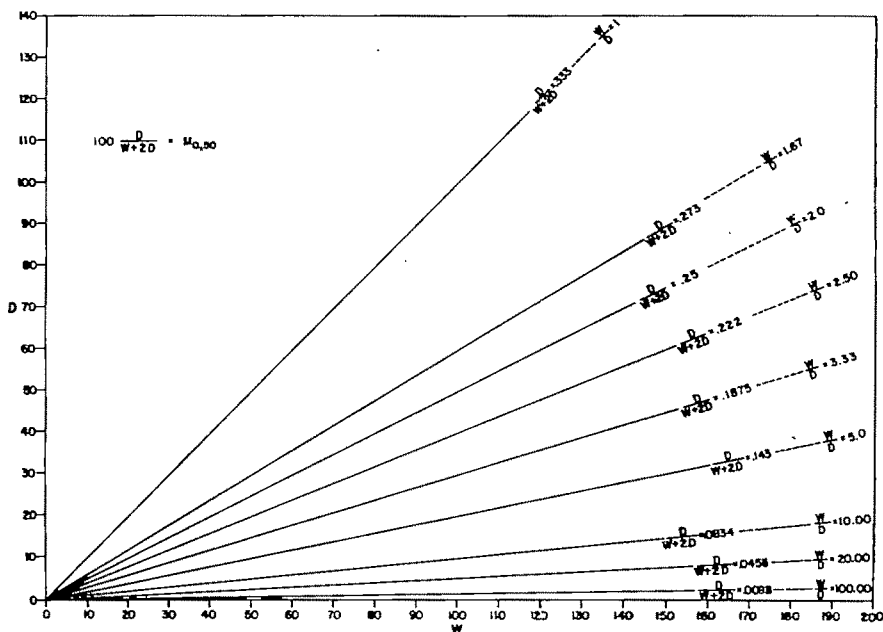


Fig. 1.

Table 1 lists values of W/D and $M_{5,75}$.

TABLE 1
Values of W/D and M , when $m_1 = 5\%$, $m_2 = 75\%$

W/D	$M_{5,75}$
1	51.8%
2	40.0
5	25.0
10	16.7
20	11.4
100	6.38

The values of W/D and M in table 1 can be plotted on Schumm's graph and will be found to fall mostly within the range of scatter of his data points, although with a steeper mean slope.

If $m_1 > m_2$, that is, if there is a *greater* percentage of silt and clay in the channel than in the bank deposits, there will be a direct relation between the width-depth ratio and M . Assuming $m_1 = 50\%$, $m_2 = 0$, then

$$W/D = f\left(\frac{50W}{W + 2D}\right). \quad (2c)$$

Table 2 lists values of W/D and $M_{50,0}$.

TABLE 2
Values of W/D and M , when $m_1 = 50\%$, $m_2 = 0$

W/D	$M_{50,0}$
1	16.7%
2	25.0
5	35.7
10	41.7
20	45.4
100	49.0

Some of the variation in M is surely due to variation in the silt and clay percentages in the bed load and bank deposits; exactly how much is not known. However, except in the special case, $m_1 = m_2$, a large proportion of the variation in M is due to variation in W/D , for purely mathematical reasons. It is therefore incorrect to correlate statistically sample values of channel width-depth ratio with the weighted mean percent silt and clay (M) as defined by Schumm. By doing so, Schumm introduced a fallacious, high degree of correlation which obscures the actual relations in nature. The fact that Schumm obtained a negative correlation between W/D and M merely indicates that in the majority of his samples the channel deposits contained less silt and clay than did the bank deposits.

Schumm states (1960, p. 178) that he was unable to obtain a significant correlation between channel width-depth ratio and any absolute measure of channel or bank deposit grain size. It is difficult to see in what way changing to percentages of silt and clay would expose a true correlation as high as -0.91 that could not be detected by using median grain size as the measure. A higher percentage of silt and clay would surely result in a smaller median size, assuming approximate log-normality. Perhaps the best explanation is that the postulated correlation between channel shape and deposit grain size is actually much lower than indicated, and Schumm's sample was too small to detect it.

Correct statistical methods exist which would permit examination of possible relations between channel shape and texture of channel and bank deposits. It would be preferable to treat measures of bed-load grain size and bank-deposit grain size as two distinct variables. Either the logarithm of the median grain size or the percent silt and clay could be used, although the former might be preferable for statistical reasons. Multiple regression analysis of channel width-depth ratio against measures of channel and bank texture would show (1) whether channel and bank texture taken together have any effect on channel cross-sectional shape; (2) whether channel texture has a greater effect on channel shape than does bank texture, or vice versa; (3) whether neither channel texture nor bank texture has any discernible effect on the channel shape characteristics.

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THE EFFECT OF SEDIMENT TYPE ON THE SHAPE AND STRATIFICATION OF SOME MODERN FLUVIAL DEPOSITS—A REPLY*

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In his discussion of the subject paper, Melton's main contention is that a large part of the variation in M (weighted mean percent silt-clay) is due to variations in channel width and depth and that the correlation between M and width-depth ratio is fallacious (Melton, 1961). These assertions will be disproved. However, Melton is basically correct in stating that the equation

$$F = 255 M^{2.1.08} \quad (1)$$

contains width and depth in disguised form, for equation 1 is equivalent to

$$F = k \left(\frac{S_c W + 2 S_b D}{W + 2 D} \right)^a \quad (2)$$

or

$$F = k \left(\frac{F S_o + 2 S_b}{F + 2} \right)^a \quad (3)$$

where F is width-depth ratio, S_c is percent silt-clay in the channel bed, S_b is percent silt-clay in the banks, W is channel width, and D is channel maximum depth. The use of equation 1, however, seems justified, for it is the best expression of the situation in nature. In defense of this choice, it is necessary to demonstrate that the percentages of silt and clay in the bed and in the banks of a stream are independent variables strongly influencing stable alluvial channel shape, that M is a meaningful parameter, and that the calculation of M does not seriously bias the results.

A multiple regression analysis involving width-depth ratio, percent silt-clay in banks, and percent silt-clay in the streambed yields the following equation:

$$F = \frac{246}{S_b^{.50} S_o^{.34}} \quad (4)$$

The coefficient of multiple correlation is 0.73, and the coefficient of multiple determination is 0.53, indicating that 53 percent of the variation of width-depth ratio from the mean is explained by the use of S_b and S_o . In a simple correlation of F and S_b the coefficient of determination is 0.39; whereas it is 0.35 in a simple correlation of F and S_o . Thus, both bank and bed sediment are important in determining channel shape. When M is correlated with F , 83 percent of the variation is explained; therefore, even if it were possible to accept Melton's assertions, only about one-third of the variation of stable channel shapes can be explained in that way.

The significance of silt-clay in the bed and banks of an alluvial channel with respect to channel shape has been demonstrated. The decision to com-

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bine bed and bank material and to calculate a weighted mean value of percent silt-clay is based on both theoretical and practical grounds. If channel shape is dependent solely on the resistance of channel bed and banks to tractive force, then equation 4 above might be adequate, although the effects of bed and bank sediment probably may not be so readily separated in nature. However, if M is not only representative of the resistance of bed and banks to erosion but also reflects the predominate type of sediment transported through the channel, then the sediment in the bed and banks should not be treated separately. That is, if sediment larger than 0.074 mm can be considered to be transported generally as bed load or at least near the bed, the percent silt-clay in the perimeter of a channel (M) would indicate the percent of total load transported in suspension. Sundborg (1956, p. 219) suggests that the finest material transported as bed load is of the size 0.15 to 0.20 mm, or twice the size of percent silt-clay as used here (0.074 mm), and Hjulström's curves (1935, p. 274) suggest quite strongly that material larger than 0.074 mm will be transported near the streambed. Exception can be taken to these statements, for the size of sediment in suspension will vary from stream to stream and from day to day on the same stream, depending on fluctuations in velocity of flow and discharge. Nevertheless, it is known that stable channels having a low width-depth ratio carry a high proportion of total sediment load in suspension, whereas those having a high width-depth ratio are characterized by large amounts of bed load (Leopold and Maddock, 1953, p. 29).

Although S_b and S_c are significantly related to F (equation 4), they are of about equal importance as shown by partial correlation. However, if it is the silt-clay forming the perimeter of the channel which is most significant, then to treat the bed and bank sediment separately will give an incorrect representation of the sediment forming the perimeter of the channel. For this reason the weighting procedure was used.

The initial studies of the relation of sediment type to channel characteristics were made along five ephemeral streams. Four of these streams are used as examples of the differences in stratification developed during aggradation of channels in the subject paper (Schumm, 1960a, fig. 2, p. 181-183). At each channel cross section visited two composite sediment samples were taken, one composed of sediments from both banks, the other from the channel floor or bed. This sampling procedure was followed because initially it seemed advisable to collect information on the sediment forming the banks as well as the bed of the channel rather than a composite sample which included material from banks and bed combined. Later the need to combine the bank and bed data was recognized, and the weighted mean percent silt-clay (M) forming the channel perimeter was calculated. It remains to be shown that the weighting procedure does not introduce a serious bias.

The calculation of a weighted mean is a standard procedure for obtaining average percentages or means from two or more groups of different importance. Croxton (1959, p. 376) describes this simple procedure and concludes as follows: "If the groups being combined are of varying importance, weights should be used. . . ." Obviously to obtain a valid measure of silt-clay in a channel perimeter from two composite samples of bank and bed sediment,

weights should be used. Thus, the weighting procedure is a standard one. If a single composite sample had been collected at each cross section, the silt-clay content of this single sample could have been used instead of M , and it would, in fact, be approximately equal to the weighted mean as calculated. Thus, if percent silt-clay forming the perimeter of a channel is measured directly by taking a composite sample along the perimeter of a channel, this measured value will be associated with a channel shape indicated by the regression line of figure 1. The calculation of M , therefore, does not affect the situation in nature that a stable channel of a given shape is found to contain a relatively constant amount of silt-clay in the channel perimeter. M simply expresses the proportion of material smaller than 0.074 mm in the channel perimeter, and as suggested above, M may be related to the proportion of silt-clay in the total sediment load moved through a channel.

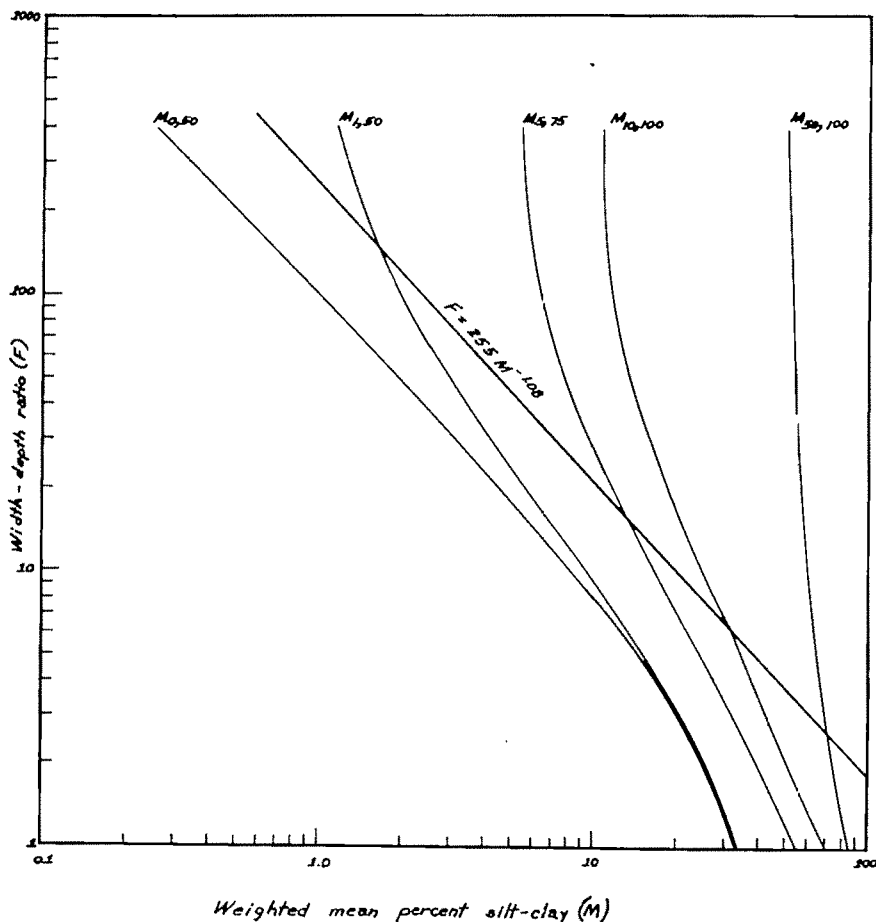


Fig. 1. Regression line illustrating relation between width-depth ratio and weighted mean percent silt-clay, $F = 255 M^{-1.04}$, superimposed on a family of curves obtained by Melton's method.

The validity of equation 1 may be further demonstrated by refuting Melton's assertion that by holding S_a and S_b constant and by varying channel width and depth it is possible to calculate values of M which will duplicate the regression line of figure 1. Melton states that calculated values of $M_{s, 75}$ "... can be plotted on Schumm's graph and will be found to fall mostly within the range of scatter of his data points, although with a steeper mean slope". However, when additional values of $M_{s, 75}$ are calculated beyond the limits presented by Melton on his table 1 but within the limits of width-depth ratio of figure 1 ($w/d = 2$ to 400), it becomes apparent that the width-depth ratio— $M_{s, 75}$ regression line—bears no relation to the line $F = 255 M^{-1.08}$. The $M_{s, 75}$ curve becomes asymptotic to the $M = 5$ ordinate, and it intersects the $M = 100$ ordinate at a width-depth ratio of 0.4, i.e., a channel four times deeper than wide. Other curves have been plotted on figure 1 for values of $M_{0, 50}$; $M_{1, 50}$; $M_{10, 100}$; and $M_{50, 100}$. All curves except that for $M_{0, 50}$ cross the regression line, but none approximate it in shape and only $M_{0, 50}$ in slope. Following Melton's reasoning it is possible to calculate values for a family of curves none of which, however, have any relation to reality.

The range of width-depth ratios and the range of percent silt-clay in banks and channel floor is considerable at the river cross sections studied (Schumm, 1960b). Therefore, according to Melton's reasoning it is surprising that the correlation between width-depth ratio and M is significant, for with the possibilities of scatter as great as indicated by the curves plotted on figure 1, no correlation should exist unless there are limits to the extent of these imposed by alluvial characteristics. That is, the physical properties of the alluvium forming the perimeter of a channel prevent the development of stable channel shapes markedly different from that indicated by the width-depth ratio— M regression line.

Data from 69 stable cross sections were the basis of the disputed regression line (fig. 1); however, data are also available for 10 additional stations which were found to be unstable, i.e., actively aggrading or degrading. The channels found to be degrading plotted below the regression line, whereas those found to be aggrading plotted above the regression line (Schumm, 1960b). Thus, the position of the points which deviate markedly from the regression line can be explained by channel instability. Since unstable sections plot away from the line, it might be assumed that they would deviate from the line in a manner similar to that suggested by the curves of figure 1. However, studies of actively degrading and aggrading channels show that as the channels become unstable the sediment forming the perimeter of the channel also changes. The percentage of silt and clay in the streambed generally increases with aggradation and decreases with degradation (Schumm, in press).

In spite of the wide scatter of points that should be produced if the points fell along a family of curves (fig. 1), a significant correlation between width-depth and M exists. An explanation as suggested by Melton is that the sample is inadequate. Although the data were collected in only seven Western States, the channel sediment and hydrologic conditions vary as follows:

Silt-clay in bank	0.5 percent to 97 percent
Silt-clay in channel	0.5 percent to 89 percent

Channel width	15 feet to 820 feet
Channel depth	1.5 feet to 18 feet
Drainage area above section	1.7 to 56,710 square miles
Mean annual flood	<450 to 48,000 cfs
Mean discharge	<30 to 5,155 cfs

Admittedly the writer has no information concerning streams with significantly greater amounts of silt-clay in the channel floor than in the banks, such as the hypothetical channel mentioned by Melton with no silt-clay in the banks and with 50 percent silt-clay in the channel. In fact, since it has been demonstrated by Hjulström (1935) that the size of sediment transported decreases inversely as the distance from the floor of the channel, it would not be expected that stable alluvial channels would contain larger sediment in the banks than in the bed or more silt-clay in the bed than in the banks.

It still remains to be demonstrated that equation 1 is valid. If equation 4 is substituted as an approximation for F into equation 3, the following is the result

$$F = k \left\{ \frac{246 \frac{S_c^{.66}}{S_b^{.50}} + 2 S_b}{\frac{246}{S_b^{.50} S_o^{.34}} + 2} \right\}^a \quad (5)$$

Substituting values of S_o and S_b into this equation results in an approximation of M determined, however, without the use of values for width and depth. When equation 5 is solved graphically for k and a the results are as follows:

$$k = 255$$

$$a = 1.1$$

Thus the coefficient and exponent of the original equation $F = 255 M^{-1.08}$ are substantially the same when the relation between width-depth ratio and the sediment forming the perimeter of a channel is determined either by using a weighting procedure involving channel width and depth or by using equation 5 above. It may be well to repeat here that M is a measure of the silt-clay exposed in the perimeter of a stream channel and that M could be obtained directly in the field by collecting a composite sediment sample along the perimeter of the channel.

Melton has also objected to the use of the silt-clay content of the alluvium rather than some measure of grain size in this paper. An analysis of variance indicates that no correlation exists between median grain size and width-depth ratio. This is not surprising considering that grain size alone is not the most important factor determining the physical properties of sediments. One need only refer to papers by Bouyoucos (1935), Trask (1959) and Dunn (1960) to be convinced of this.

Unquestionably much remains to be done before a full understanding of the effects of sediment on stream character can be obtained, but there is no question that an exchange such as this is helpful in stimulating ideas and doubts about field techniques and the problem in general.

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Vth CONGRESS OF THE INTERNATIONAL ASSOCIATION FOR QUATERNARY RESEARCH (INQUA)

The International Association for Quaternary Research (INQUA) will meet in Poland during the late summer of 1961. The Congress, which meets every four years, will be preceded by an excursion starting from Warsaw on August 27. The first meeting of the Congress will take place on September 2, and the last meeting on September 7. A post-Congress excursion will be held from September 7 to 21 and will visit the main localities containing Polish Quaternary deposits.

INQUA was first organized during an international geological meeting in Copenhagen in 1928 for the purpose of approaching Quaternary problems on an interdisciplinary level particularly in the fields of geology, archaeology, climatology, and chronology. Although the Congress has been attended primarily by Europeans, it is international and non-Europeans are urged to attend.

All persons interested in the 1961 Congress in Poland may obtain more detailed information by writing to the following:

Professor Rajmund Galon
Secretary General, INQUA
Geographical Institute
University
Toruń, Poland

XVth INTERNATIONAL CONGRESS OF LIMNOLOGY

The XVth International Congress of Limnology will be held at the University of Wisconsin, Madison, Wisconsin, August 20-25, 1962. The Congress is sponsored in North America by the American Society of Limnology and Oceanography with the cosponsorship of the National Academy of Sciences-National Research Council and Societas Internationalis Limnologiae. All previous congresses, held triennially, have been in Europe. Inquiries should be addressed to: The XVth International Congress of Limnology, c/o Dr. John C. Wright, Birge Hall, University of Wisconsin, Madison 6, Wisconsin.

Sessions on the world's great lakes, latitudinal limnology, decomposition, and problems common to limnology and oceanography are among those planned. Excursions are scheduled for participants to various aquatic areas and research centers of North America. The Executive Committee for the Congress is: Drs. Arthur D. Hasler, Chairman, John C. Wright, Executive Secretary, George H. Lauff, Treasurer, Kenneth D. Carlander, David G. Frey, and Donald S. Rawson.

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APRIL 1961

THE INDEPENDENCE DIKE SWARM IN EASTERN CALIFORNIA*

JAMES G. MOORE¹ and CLIFFORD A. HOPSON²



ABSTRACT. A dike swarm up to 15 miles wide and at least 85 miles long cuts northwestward across the Sierra Nevada, Inyo Range, and Argus Range in eastern California. The dike rocks range from lamprophyre to granodiorite porphyry, the more mafic types predominating. The dikes are probably of Cretaceous age, for they intrude some granitic plutons of the Cretaceous Sierra Nevada batholith but are truncated by others. The dikes in the Sierra Nevada were metamorphosed by the younger granitic intrusives. In the Inyo and Argus Ranges the dikes are hydrothermally altered, but otherwise unmetamorphosed.

Two sequences of granitic intrusion in the Sierra Nevada batholith (Mount Pinchot quadrangle) can be separated by the dike swarm. Each sequence apparently began with the emplacement of mafic granodiorite and concluded with alaskite; succeeding intrusions in each sequence were progressively more felsic. Two cycles of differentiation seem indicated. Chilled dike margins where the swarm cuts earlier plutons indicates that a significant time interval separated emplacement of pre-dike and post-dike plutons.

The dike swarm shows no apparent offset where it crosses Owens Valley. This argues against suggested major strike-slip faulting along the line of Owens Valley since Cretaceous time.

INTRODUCTION

A group of predominantly mafic dikes in the Sierra Nevada, Inyo Range, and Argus Range in eastern California forms a large northwest-trending swarm traceable for 85 miles. The dikes have already been described in isolated localities, but a dike swarm of regional extent has not previously been recognized. The name "Independence dike swarm" is proposed, from the town of that name in Owens Valley on line with the swarm (fig. 1).

The dike swarm is of interest not only as a major petrologic and structural feature but also as a means of separating two sequences of granitic intrusions in the Sierra Nevada batholith.

We have investigated the dikes in detail in the Mount Pinchot quadrangle in the Sierra Nevada during three and a half summers of mapping (Moore, 1954; and a report in preparation). The dikes of the Inyo Range and Alabama Hills were studied by us only in reconnaissance. E. M. MacKevett, C. W. Merriam, C. A. Nelson, W. C. Smith, D. C. Ross, and W. E. Hall have generously supplied additional data on the dikes in the Inyo and Argus Ranges, and P. C. Bateman on the dikes in the Sierra Nevada north of the Mount Pinchot quadrangle.

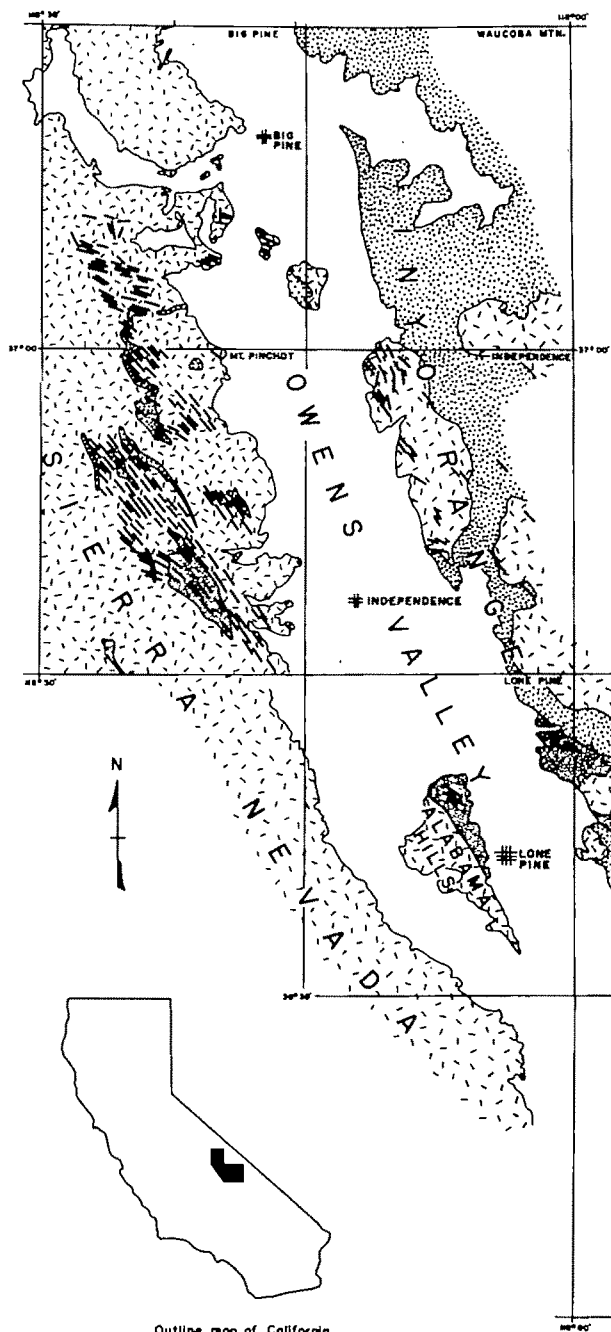
EXTENT OF THE DIKE SWARM

The dikes are most abundant and best exposed along the high crest of the Sierra Nevada. The main group, centering in the Mount Pinchot quadrangle, consists of hundreds of steeply dipping dikes striking northwestward across

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¹ U. S. Geological Survey, Menlo Park, California.

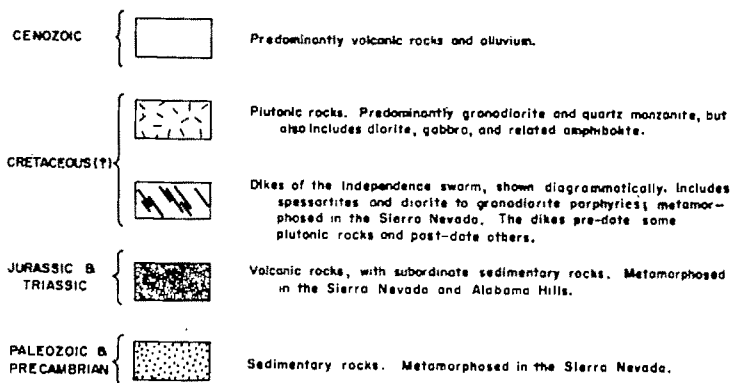
² The Johns Hopkins University, Baltimore, Maryland.



Outline map of California,
showing location of the Independence area.

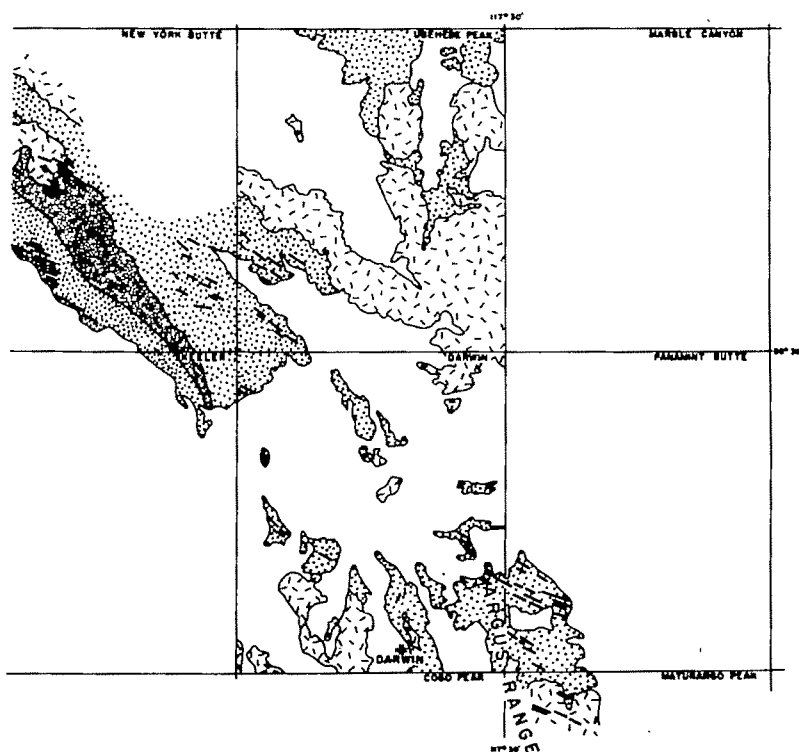
Fig. 1. Generalized geologic map

GENERALIZED GEOLOGIC MAP
OF THE INDEPENDENCE DIKE SWARM



0 10 20 miles

Quadrangle names appear in upper right hand corners.



showing the Independence dike swarm.

the quadrangle in a swarm at least 9 miles wide (fig. 2). Northward the dike swarm extends into the Big Pine quadrangle (P. C. Bateman, 1958, written communication), but there it is truncated on the northwest by younger granitic intrusions. The possible northwestward continuation of the dikes into the Mount Goddard quadrangle (west of the Big Pine quadrangle) has not been investigated.³

In the Inyo Range the dikes have been mapped only in isolated localities: in the Burgess Mine area, west-central New York Butte quadrangle (E. M. MacKevett, 1958, written communication), in the Cerro Gordo mine area, southwestern New York Butte quadrangle (C. W. Merriam, 1958, written communication; Page, 1951, p. 24), in the Santa Rosa mine area, northwest Darwin quadrangle (MacKevett, 1953), and in the Independence quadrangle (D. C. Ross, 1959, written communication). C. A. Nelson (written communication, 1959) reports northwesterly-trending dark-colored dikes in the extreme southwestern corner of the Waucoba Mountain quadrangle. We have mapped the dikes in reconnaissance along the west flank of the Inyo Range in the New York Butte and Lone Pine quadrangles, and in the Alabama Hills, Lone Pine quadrangle.

Nearly 15 miles of alluviated valley separates the dike swarms in the Sierra Nevada and Inyo Range. Fortunately an upfaulted block of crystalline bedrock, the Alabama Hills, is in the valley directly on strike with both dike swarms. Here similar northwest-trending dikes link the Sierra Nevada and Inyo swarms.

Similar dark-colored dikes, striking northwestward on line with the Sierra Nevada-Inyo Range swarm, occur in the Argus and other desert ranges to the southeast: in the southwest corner of the Panamint Butte quadrangle and in the northwest corner of the Maturango Peak quadrangle (W. E. Hall, 1958, written communication), in the Darwin quadrangle (Hall and MacKevett, 1958), and in the southwest corner of the Ubehebe Peak quadrangle (McAllister, 1956). The dikes near Darwin, called andesite porphyry by Hall, are similar to those in the Inyo Range which we call diorite porphyry. The possible southeastward continuation of the dikes beyond those shown in the Maturango Peak quadrangle has not been investigated.⁴

The map of the dike swarm (fig. 1) has been compiled from the above sources, with the geologic map of the Owens Valley region (Bateman and Merriam, 1954) serving as a base.

THE DIKE ROCKS

The Independence dike swarm, on both sides of Owens Valley, consists predominantly of dark-colored dike rock but includes leucocratic types as well. The swarm is, in fact, a dike series, with a wide range of intermediate rock

³ In the summer of 1960 Moore and F. C. Dodge mapped predominately northwest-trending dikes through the Mount Goddard quadrangle (bordering the Big Pine quadrangle on the west) and into the Blackcap Mountain quadrangle (bordering the Mount Goddard quadrangle on the west).

⁴ After this paper went to press G. I. Smith (Geol. Soc. America Program, 1960 Annual Meetings, Denver, p. 211) reported a similar dike swarm cut by the Garlock fault, which is probably the southeastern continuation of the Independence swarm. Total length of the Independence swarm plus that mapped by Smith is greater than 160 miles.

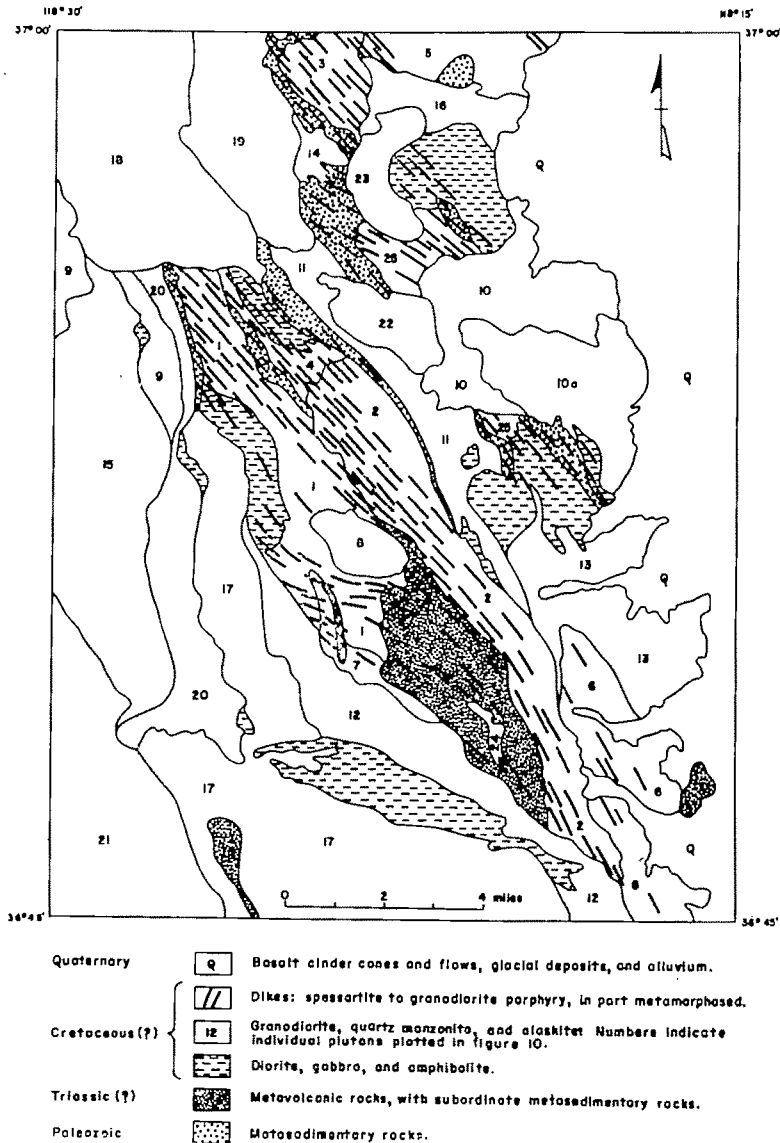


Fig. 2. Generalized geologic map of the Mount Pinchot quadrangle, California.

types. Lamprophyre, most commonly spessartite,⁵ is the mafic end member of the series, and granodiorite porphyry is the usual felsic end member. The nearly complete range of intermediate types (chiefly diorite and quartz diorite

⁵ Following Rosenbusch (1887, p. 308-309), lamprophyre is used here to mean a dark-colored, fine-grained or porphyritic rock, which, if porphyritic, is characterized by two generations of ferromagnesian minerals but not of feldspar. The texture is typically panidiomorphic. Spessartite is the variety carrying sodic plagioclase and hornblende and/or augite as the principal primary minerals.

porphyries) suggests that all members of the dike swarm share a close genetic relationship. Similar dike series are known from Washington (Waters, 1927), Scotland (Flett, 1905; Bailey and Maufe, 1916; King, 1937), and Ireland (Reynolds, 1931).

The dike rocks of the Inyo Range and Alabama Hills are similar petrographically and will be described together. Those in the Sierra Nevada have been deformed and recrystallized; they are described separately.

Inyo Range and Alabama Hills.—The dikes in the Inyo Range cut Paleozoic and Triassic sedimentary and volcanic rocks. Locally they also intrude Cretaceous (?) granitic rocks (MacKevett, 1953, p. 5), and are nonconformably overlain by Pliocene (?) pyroclastic rocks. Hall and MacKevett (1958, p. 13) consider the dikes in the Darwin quadrangle to be Cretaceous (?).

Large local swarms of dikes are found along the foot of the range 6 miles north-northeast and 8 miles southeast of Lone Pine. Spessartite, diorite porphyry, and quartz diorite to granodiorite porphyry are the principal dike rocks, the darker-colored types being most abundant. These dikes average 2 feet in width, sharply transect the country rock, and display chilled margins.

The dark-colored dike rocks are generally porphyritic, with hornblende or augite phenocrysts. These mafic minerals, now almost completely altered, were originally present in the groundmass as well, giving the two-generation texture typical of lamprophyres. Plagioclase is also common as phenocrysts,

TABLE 1
Modal analyses of dike rocks, Inyo Range and Alabama Hills

Minerals	D-1	D-2	D-11
Plagioclase (altered)	42.3	42.6	35.5
Quartz	2.4	2.8	
Hornblende	7.2		30.4
Montmorillonoid			15.6
Epidote	19.4	24.0	15.1
Chlorite	18.0	22.3	
Sphene	5.5	1.3	
Leucoxene			3.4
Apatite	0.8	0.8	
Carbonate minerals	tr.	6.1	
Opaque accessories	4.4	0.1	
Total vol. %	100.0	100.0	100.0
Points counted	1098	1066	1048

D-1 Spessartite. West flank of the Inyo Range, north of Dolomite Station on the Southern Pacific Railroad.

D-2 Spessartite. Crest of the Inyo Range, two miles southeast of New York Butte. (Abundant primary hornblende and biotite in D-1 and D-2 is almost entirely altered to chlorite and epidote).

D-11 Spessartite. North end of the Alabama Hills.

Note: The above three modal analyses have low accuracy due to the extremely fine-grained and altered condition of the rocks. X-ray data suggest that the quartz content of D-1 and D-2 is higher than shown, also that considerable muscovite is present (mainly as a fine, "sericitic" alteration of the plagioclase). Staining and X-ray data also suggest the presence of potassium feldspar in all three rocks.

especially in the more felsic dike rocks. Most of the dike rocks are so intensely altered that primary minerals are scarcely recognizable. The plagioclase (originally sodic andesine) is strongly saussuritized, and the ferromagnesian minerals are decomposed to chlorite, epidote, and magnetite or hematite. Sphene and ilmenite are altered to leucoxene. Carbonate minerals have extensively replaced primary minerals in many dikes. Modal analyses of two typical spessartites from the Inyo Range are given in table 1. The more felsic dike rocks are as intensely altered as the mafic dikes. They consist of sericitized and saussuritized feldspar (chiefly sodic plagioclase), quartz, and chloritized biotite or hornblende.

Northwest-trending dikes in the Alabama Hills are as much as 30 feet wide but average 3 feet. These dikes have chilled margins and they cut Triassic (?) metavolcanic rocks in the northern part of the hills. None, however, were observed to cut the Cretaceous granitic rocks, though a detailed search was not made. The age of the dikes in the Alabama Hills, therefore, can be placed no closer than probably post-Triassic.

Petrographically the dike rocks of the Alabama Hills closely resemble those of the Inyo Range. They range from spessartite to granodiorite porphyry, the darker-colored types predominating. The mode of a typical spessartite appears in table 1. The spessartites have the panidiomorphic texture typical of lamprophyres, with two generations of euhedral hornblende (fig. 8). Plagioclase (oligoclase to sodic andesine), green hornblende, and probably biotite were the primary dike minerals, but alteration has profoundly modified the rock. The plagioclase is intensely saussuritized, and hornblende is partly changed to pale grayish green actinolitic amphibole with patches of greenish montmorillonoid. Granules of secondary epidote, patchy aggregates of fine green montmorillonoid, chlorite, leucoxene, and tiny needles of apatite are disseminated throughout the groundmass.

The intermediate and felsic dike rocks are mineralogically similar to the spessartites, but they have smaller amounts of dark minerals, and plagioclase phenocrysts are more abundant. Spherulitic granodiorite porphyry is the most felsic end member of the dike series in the Alabama Hills. The more felsic dike rocks, too, are strongly altered, so that even the most felsic appear dark colored because of the finely disseminated epidote, chlorite, and sericite.

Alteration of the dike rocks in the Inyo Range and the Alabama Hills was probably caused by residual fluids during the final stage of dike crystallization. The alteration is not localized along later fractures but is dispersed throughout the interior of each dike, decreasing in intensity toward the chilled margins. The abundance of carbonate minerals in many of these altered dike rocks indicates that CO₂-rich fluids played an important role in the alteration.

Sierra Nevada (Mount Pinchot quadrangle).—West of Owens Valley the dike swarm continues northwestward from the Alabama Hills with no apparent offset, cutting granitic rocks of the Sierra Nevada batholith and associated septa of metamorphic rocks. The main swarm trends diagonally through the center of the Mount Pinchot quadrangle, crossing the Sierra crest in the vicinity of Mount Baxter. It is magnificently exposed in the bare, glacially scoured basins at Twin Lakes, Woods Lake (figs. 3 and 4), and along the up-



Fig. 3. Mafic dikes east of Woods Lake in the west-central Mount Pinchot quadrangle. Dikes in foreground are about 2 feet thick and dip steeply northeast.

per South Fork of Woods Creek. Farther north a second large concentration of dikes (fig. 5) crosses the Sierra crest at Taboose Pass (Knopf and Kirk, 1918, p. 71). All dikes are sharply intrusive, dilating transected planar structures (fig. 6), and displaying chilled margins.

In the Mount Pinchot quadrangle the following relations are important: granitic rocks of the Sierra Nevada batholith are intrusive into metasedimentary rocks of probable Paleozoic age, metavolcanic rocks of probable early Mesozoic age, and gabbroic and dioritic rocks of mixed origin, also of probable Mesozoic age. The granitic rocks form a mosaic of 26 elongate north- to northwest-trending plutons, commonly separated by thin concordant septa of metamorphic and dioritic rock (fig. 2). The dikes cut the metamorphic rocks and some of the granitic plutons, but are truncated by other plutons. Thus the dikes are younger than some plutons but older than others.

Radiometric dating of plutonic rocks in the eastern Sierra⁶ indicates the main bulk of Sierran granitic rocks to be of Late Cretaceous age. Granitic rocks along the western foothills of the Sierra, however, are Late Jurassic (Curtis, Evernden, and Lipson, 1958, p. 10). Granitic rocks in the Mount Pinchot quadrangle have not been dated radiometrically, but their close rela-

⁶ Granitic rocks along the Sierra Nevada crest near Bishop (30 miles north of the Mount Pinchot quadrangle), dated by the zircon lead-alpha method, range in age from 90 to 111 m.y. (Faul and others, 1954, p. 265). Granitic rocks in the Yosemite region (70 miles northwest of the Mount Pinchot quadrangle), dated by the K^{40}/A^{40} age of their biotites, range from 77 to 95 m.y. (Curtis, Evernden, and Lipson, 1958, p. 12).



Fig. 4. Mafic dikes cutting quartz monzonite near Twin Lakes, Mount Pinchot quadrangle. Note branching and rejoining of dikes. Hammer (center) gives scale.

tionship to eastern Sierra rocks of known age indicates that they, too, are Cretaceous. The dikes, therefore, bracketed by these granitic rocks, are probably also Cretaceous.

Though little change is evident from the map pattern, many of the dikes are strongly deformed and recrystallized. They have: (1) developed internal schistosity; (2) been broken and boudinaged; (3) been mobilized and re-injected into their granitic wall rock; and (4) been partly granitized.

Internal shearing has formed a schistosity within the dikes, commonly subparallel to their contacts. The schistosity does not extend out into the wall rock. The dikes, incompetent relative to the granitic wall rock, were evidently zones of weakness along which considerable differential movement in the area was localized. In the Woods Lake region the schistosity pattern is shaped like a reversed integral sign, being oblique in the interior but curving around parallel to the contacts in the marginal portions of the dikes. The orientation of oblique schistosity in nearly every dike indicates left-lateral movement. It is not clear whether the schistosity was formed during the closing stage of dike solidification or at some later time. Cataclastic texture is lacking, showing that recrystallization outlasted or postdated the movement.

Other movements are clearly later than dike intrusion. Plastic flow of the granitic host rock has locally disrupted the dikes, leaving trains of dismembered dike fragments similar to boudins. More rarely, these disrupted dikes have themselves been remobilized, injecting the plastically deformed granitic rock. This is shown by delicate dikelets, which extend from the boudins but

which are themselves not deformed by the flow which disrupted the main dike. Evidently after the plastic granitic rock had acquired sufficient rigidity to fracture, the recrystallizing mafic rock was squeezed into small dislocations.

Disruption of the dikes was locally accompanied by granitization. Parts of some dikes are replaced by light-colored, coarser, more granitic-appearing rock. Whole segments of other dikes are replaced, leaving only a nebulous outline and isolated skialiths to mark the original structure. Elsewhere replacement followed the dike margins, leaving the interior unaffected. Perhaps the dike contacts formed a channelway for the granitizing solutions.

TABLE 2

Modal analyses of dike rocks, Sierra Nevada (Mount Pinchot quadrangle)

Minerals	MP-52b	B-533	B-820b	B-428	B-727a
Plagioclase	38.7	44.7	45.6	59.6	53.5
Potassium feldspar					7.7
Quartz	0.9	1.8	3.2	1.1	10.4
Hornblende	50.5	34.9	29.5	30.1	14.8
Biotite	8.8	13.1	15.5	3.6	10.0
Epidote			1.2		0.3
Sphene	1.0	1.2	1.5	2.7	1.7
Apatite	0.1	0.9	1.3	0.6	0.7
Zircon		0.2		tr.	tr.
Magnetite		3.2	2.2	2.3	0.9
Total vol. %	100.0	100.0	100.0	100.0	100.0
Points counted	1058	1045	1054	1123	1083

MP-52b Meta-spessartite (relict texture), Woods Lake Basin.

B-533 Meta-spessartite. One-half mile ENE of Pyramid Pk.

B-820b Meta-spessartite. Cardinal Mountain (east ridge).

B-428 Meta-spessartite (?). Charlotte Lake.

B-727a Mafic meta-granodiorite porphyry, Taboose Pass.

The mafic dikes, which greatly predominate over the felsic types, are green hornblende-plagioclase rocks, with biotite and subordinate quartz as common accessories. The plagioclase is calcic oligoclase to sodic andesine, unzoned in some dikes and with weak progressive zoning in others. Modes of typical mafic dike rocks from this area are given in table 2.

With few exceptions these dike rocks have been partially to completely recrystallized. Relict lamprophyric texture survives in a few mildly recrystallized dikes (fig. 7), but most dikes have been transformed into granoblastic mosaics, either hornfelsic or foliated. Large "clots" of small hornblende granules are the recrystallized relics of original mafic phenocrysts.

In general the primary textures have survived better in the felsic dike rocks. In the granodiorite porphyries the groundmass is recrystallized to a fine granoblastic mosaic of feldspar and quartz, but the original plagioclase phenocrysts are well preserved. All the recrystallized dike rocks are clean and fresh, in contrast to the strongly altered dike rocks of the Inyo Range and Alabama Hills.



Fig. 5. Taboose Pass (foreground) and Goodale Mountain along the High Sierra crest, Mount Pinchoi quadrangle. Abundant mafic dikes, trending northwest, are visible at the upper and lower right and at the center of the photograph (arrows). These dikes are truncated by a younger quartz monzonite pluton at Goodale Mountain (dashed line).

The mafic dike rocks were originally spessartite, rather than diabase. This is shown, in the least-recrystallized dikes, by the relict panidiomorphic, rather than ophitic texture, and by the sodic, rather than calcic plagioclase. Moreover, only the most mafic dike rocks are chemically similar to diabase.

DIKE CORRELATION

The following data suggest that the dikes on both sides of Owens Valley are of approximately the same age and belong to a single great swarm:

(1) The northwest-trending dikes in the Sierra Nevada, the Alabama Hills, and the Inyo Range are aligned, and are separated only by the alluvium in Owens Valley.

(2) The dikes on both sides of the valley are of the same rock types. They range from spessartite to granodiorite porphyry (or the metamorphosed equivalents), evidently as a continuous dike series. Relict textures and mineralogy indicate that before they were altered and metamorphosed they were very similar.

(3) The dikes from the three areas all fall in the same general composition range. In lieu of chemical analyses of the dike rocks, their compositions are compared by their specific gravities and by the refractive index of their fused beads (fig. 9). The latter, an approximate measure of SiO_2 content

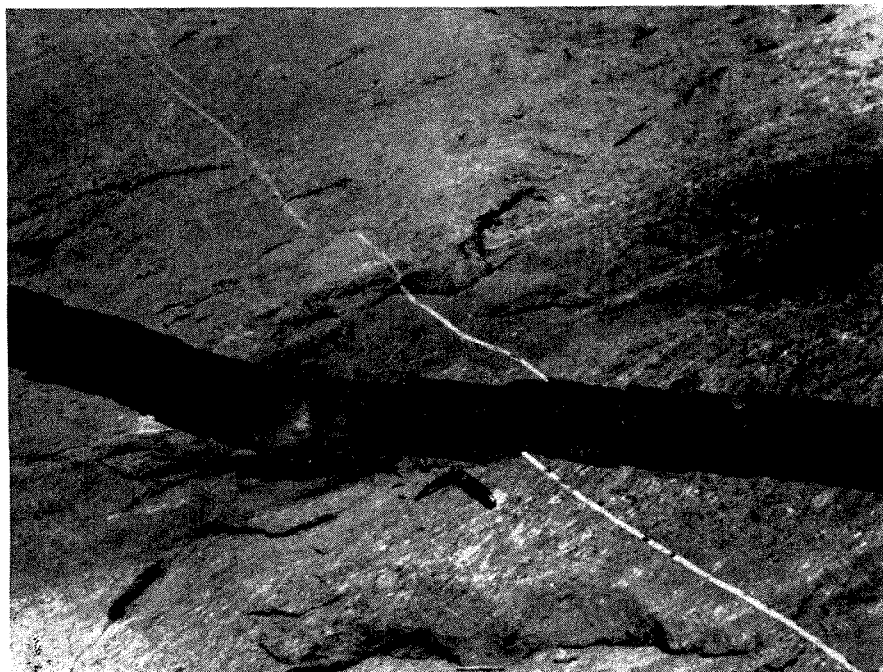


Fig. 6. Mafic dike in west-central Mount Pinchot quadrangle cutting metamorphosed volcanic breccia. The dike offsets a thin aplite dike and dark bands in the host rock perpendicular to its walls. Note matching walls, flow structure, and finer-grained, chilled margins.

(Mathews, 1951), suggests a range from about 48 percent silica (mafic dikes) to 75 percent silica (felsic dikes).

The dike ages are not in conflict with the correlation, but neither are they closely enough known to support it. The dikes in the Sierra are probably Cretaceous, those in the Inyo Range are probably post-Early Cretaceous but pre-Pliocene, and those in the Alabama Hills are probably post-Triassic.

Other mafic dikes, of decidedly different age and origin, occur near Mount Clarence King in the Mount Pinchot quadrangle. These are small, gently dipping apophyses from dioritic septa. Contact relations show these septa to be older than the granitic rocks they locally intrude. Evidently during granitic intrusion the dioritic wall rock was softened, perhaps partially melted, and squeezed into dislocations in the solidifying granite. These mobilized dioritic dikes are easily distinguished from dark-colored dikes of the northwest-trending swarm. They are not considered in the remaining discussion.

Probably all dikes of the main swarm in the Mount Pinchot quadrangle were nearly contemporaneous. In addition to forming a unified dike series no evidence for more than one period of dike emplacement has been found. For instance, there are no plutons which truncate dark-colored dikes but which are in turn cut by other dark-colored dikes. Because of the large number of plutons in the quadrangle (at least 26), and the great abundance of dikes, there would

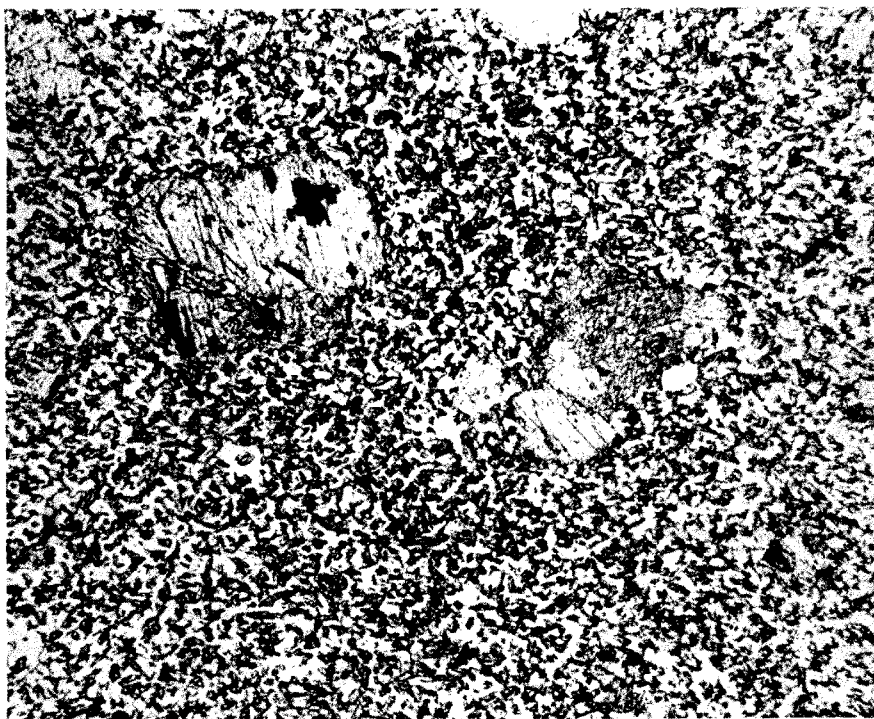


Fig. 7. Photomicrograph of a mafic dike rock from near Twin Lakes, Mount Pinchot quadrangle. Large relict phenocrysts of green hornblende, set in a recrystallized granoblastic matrix of green hornblende and andesine. Plain light, X 30.

be ample opportunity for relationships of this sort had there been more than one stage of dike intrusion.

METAMORPHISM OF THE DIKES

The deformation, recrystallization, and granitization of the dikes where they penetrate the Sierra Nevada batholith is attributed to the emplacement of the younger plutons. In the Mount Pinchot quadrangle 8 plutons, totaling about 40 square miles of present surface area, predate the dikes and serve as hosts for them. Eighteen other plutons, totaling about 120 square miles, probably postdate the dikes. Several of the plutons (numbers 10, 14, 16, and 18 of figure 2) clearly cut the mafic dikes. At the contact the dikes are sharply truncated, more coarsely recrystallized, included as broken fragments within the pluton, and cut by aplitic dikes satellitic to the pluton. However, the only criterion for other plutons' being younger than the dikes is the absence of dikes cutting these plutons.

The plutons were probably emplaced forcibly, pushing aside the wall rocks to make room for themselves. The northwest-trending, steeply isoclinally folded metamorphic rocks and elongate earlier plutons were split apart, like the pages of a book, by each succeeding pluton. Thus the earlier rocks were considerably squeezed and deformed during emplacement of the younger plutons. This

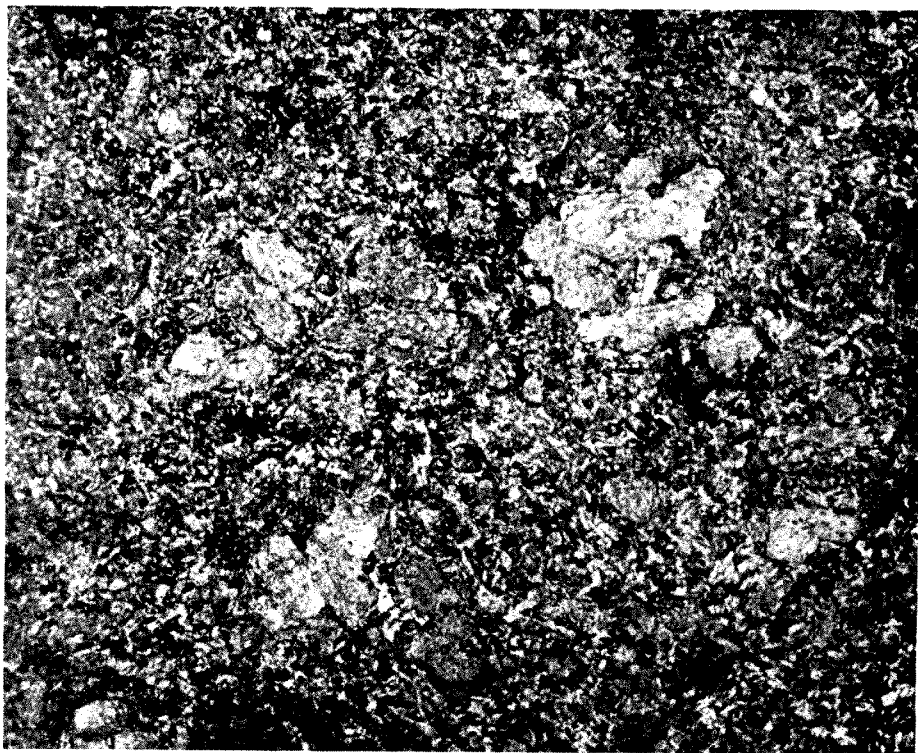


Fig. 8. Photomicrograph of a mafic dike rock from the northern end of the Alabama Hills. Green hornblende phenocrysts, set in a fine-grained matrix of hornblende, plagioclase, montmorillonoid, epidote, and leucoxene. The hornblendes are partially altered to pale grayish green actinolite amphibole, and the plagioclase is strongly saussuritized. Plain light, X 30.

deformation, together with the heat and fluids escaping from the younger intrusions, seems adequate to explain the metamorphism of the dikes.

The older granitic rocks show considerable evidence of strain, cataclasis, and recrystallization. In contrast, the primary hypidiomorphic texture of the youngest plutons remains nearly unchanged. There is no simple correlation between intensity of dike metamorphism and proximity to the contacts of younger plutons. All dike samples collected near younger plutons were indeed strongly recrystallized, and the least recrystallized specimens were quite distant from such contacts. Many intensely deformed and recrystallized dikes, however, also occur far from exposed younger plutons. This is not surprising, for the older plutons must have been squeezed, stretched, and deformed throughout to have accommodated such a vast bulk of younger intrusions.

A BREAK IN THE SIERRA NEVADA PLUTONIC SEQUENCE

In the Mount Pinchot quadrangle two groups of granitic plutons are separated by the dike swarm. The dikes have chilled margins against the earlier plutons. Furthermore, in both the pre-dike and post-dike groups of plutons the composition ranges progressively from mafic granodiorite to alask-

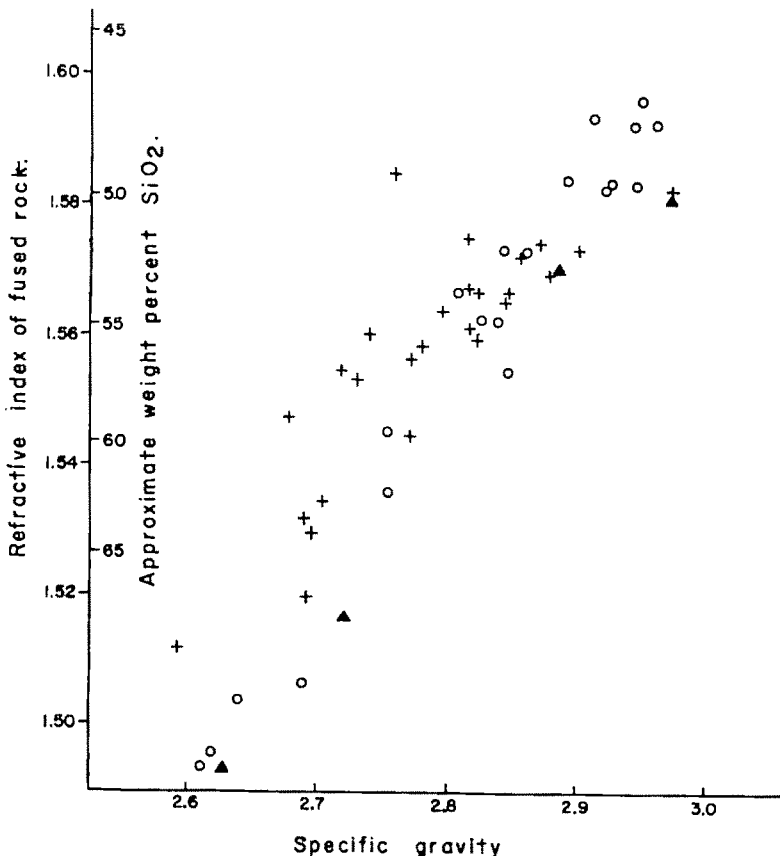


Fig. 9. Specific gravity of dike rocks plotted against the refractive index of the fused rock which is an approximate measure of percent silica (Mathews, 1951). Dikes from the Mount Pinchot quadrangle shown by circles, dikes from the Inyo Range by crosses, and dikes from the Alabama Hills by triangles.

ite, suggesting the possibility of two distinct sequences of magmatic differentiation in the area. These features indicate a larger break in time than is probably represented by intervals between successive plutons within each of the two series.

Of the 26 plutons mapped in the quadrangle 8 are older than the dikes and 18 are probably younger. The relative ages of contiguous plutons are generally shown by intrusive relations at their contacts. The known relative ages of pre-dike and post-dike plutons are shown graphically in figure 10. A complete sequence of intrusion cannot be established, because the relative ages of plutons not in contact are generally indeterminate.

Plutons of both the pre-dike and post-dike groups become more felsic with decreasing age. They are increasingly enriched in quartz and potassium feldspar (fig. 10), and show a progressively decreasing color index. This trend cannot be definitely established without knowledge of the complete sequence of intrusions (rather than of those just in mutual contact), but the fragmentary

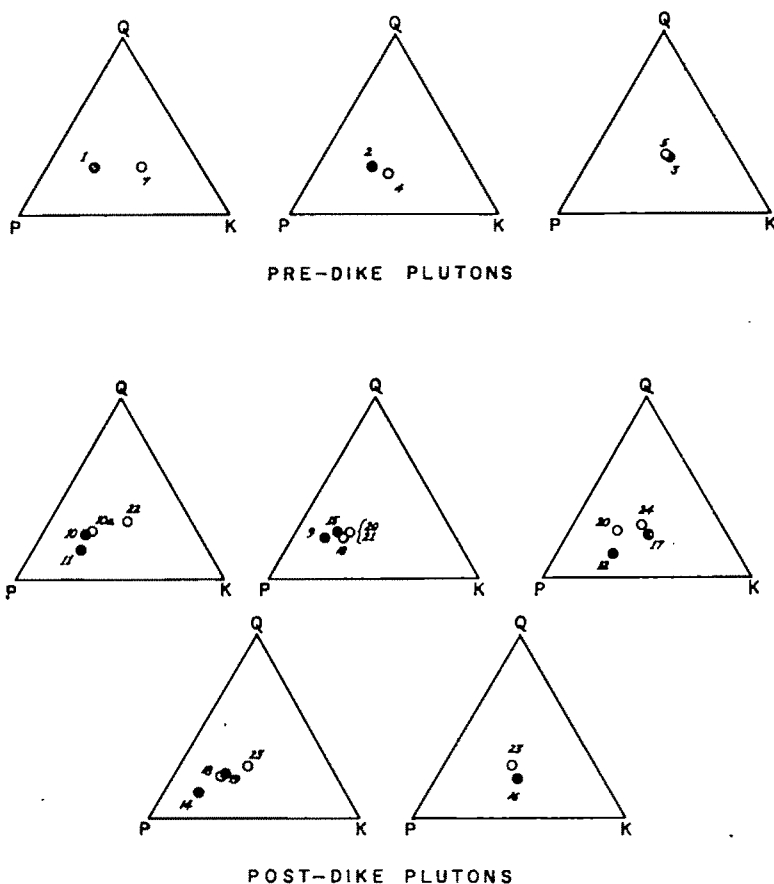


Fig. 10. Plots showing the change of average modal composition in successively younger plutons. Plotted in each triangle are only those plutons whose relative ages are known from observed contact relations. Solid circles represent the oldest pluton, circles with dot the intermediate pluton, and open circles the youngest pluton(s) of each group of plutons in contact. The relative age of two plutons in different triangles is generally unknown (e.g. a pluton plotted as a solid circle in one triangle may be younger than one plotted as an open circle in another triangle). Numbers correspond to plutons shown in figure 2. The plots show the general tendency for successively younger pre-dike and post-dike plutons to become progressively enriched in quartz and potassium feldspar. P, plagioclase; Q, quartz; K, potassium feldspar.

evidence available is strongly suggestive. Only one important reversal of this trend (fig. 10, plutons 17 and 20) is evident.

Only when the pre-dike and post-dike groups of plutons are considered separately does the trend for plutons to become increasingly more felsic with decreasing age become evident. If all plutons in the quadrangle were considered as a single group, numerous cases would occur in which the more felsic plutons were intruded by more mafic ones. Hence, two sequences of plutons are apparently present, each progressing from mafic granodiorite through increasingly more felsic rocks to alaskite. The dike swarm separates these two sequences.

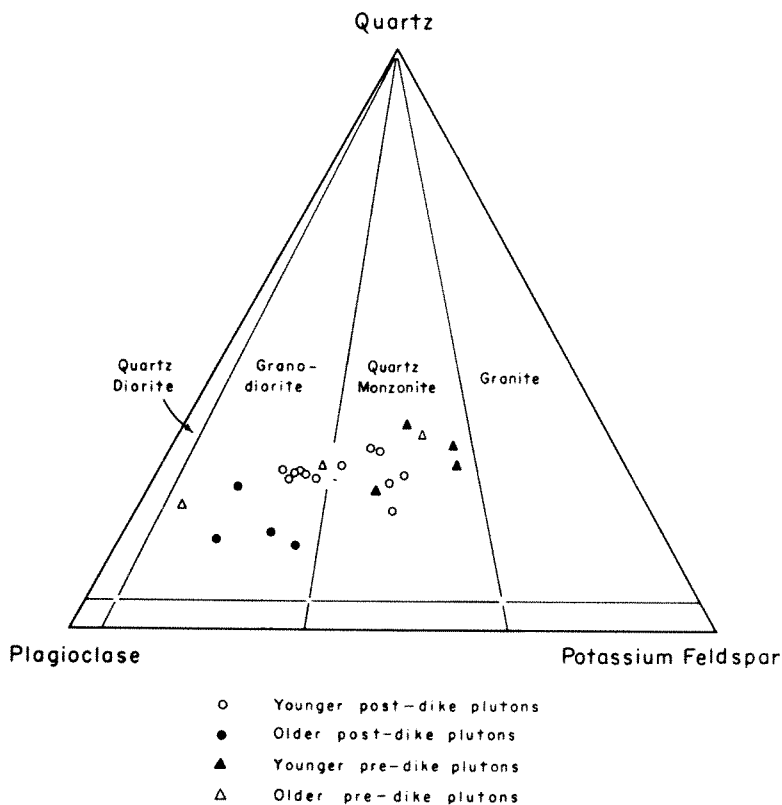


Fig. 11. Plot showing average modal composition of plutons in the Mount Pinchot quadrangle. Note the wide compositional difference between the younger pre-dike plutons and the next youngest intrusives, the older post-dike plutons. This difference emphasizes the break between the pre-dike and post-dike sequences of intrusion. Rock classification used here is modified from Johannsen (1931).

The possibility of two periods of granitic differentiation is thus indicated. It may also be significant that the break between the two sequences is marked by the greatest difference in composition of the plutons. The younger pre-dike plutons are in general the most silicic and potassic of all the granitic rocks, whereas the next succeeding group of intrusions, the older post-dike plutons, are in general the most mafic (fig. 11). This fact is difficult to reconcile if all the granitic rocks of the area represent but a single cycle of differentiation.

Metamorphosed mafic dikes have proved useful in other areas in establishing two periods of orogeny. In southwestern Finland, Sederholm used metabasaltic dikes to distinguish older and younger Archean granites (1926, p. 31-36). The dikes, intensely deformed and recrystallized during migmatization associated with formation and emplacement of younger granite, evidently mark a major break in the plutonic history of the Finnish Precambrian. Two periods of regional metamorphism and migmatization were similarly deciphered in the gneiss complex of West Greenland (Ramberg, 1948) and in the Lewisian gneisses in the North-West Highlands of Scotland (Sutton and

Watson, 1951). The dikes in each area were originally diabase, showing chilled margins against their crystalline wall rocks. Erosion to shallow depth, tension, and tapping of simatic material evidently separated periods of major plutonic activity, indicating a time interval of considerable duration between them.

In the Sierra Nevada, mafic dikes with chilled margins are similarly deformed and recrystallized, but two major orogenies are not involved. The time interval separating pre-dike and post-dike plutons was relatively short, probably only a part of a geologic period.

STRIKE-SLIP FAULTING ALONG OWENS VALLEY

Major strike-slip faulting along the line of Owens Valley has been suggested by Hill (1954, p. 10). The long, linear shape of the valley, the approximate parallelism of the valley with the San Andreas fault, and the observed strike-slip movement along small faults at the time of the 1872 earthquake (Hobbs, 1910, p. 379), suggest this possibility. But the continuation of the dike swarm along the same strike across Owens Valley without obvious offset seems to preclude strike-slip displacement of great magnitude since Cretaceous time, probably not exceeding a few miles at most.

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SEDIMENTARY XENOLITHS AND DOLERITE PATCH PEGMATITES FROM AN ANALCITE BASALT INTRUSION

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ABSTRACT. Reaction of sandstone and shale xenoliths with alkali basalt produced trachyte, dolerite, and dolerite-pegmatite modifications adjacent to the xenoliths. Reaction products are shown to represent modified host magma and to correspond chemically to possible differentiates of uncontaminated alkali basalt. The interplay of several processes prevents quantitative evaluation of the contribution of each to differentiation, but the following sequence of events is postulated to explain the origin of reaction products: upon immersion of cold xenoliths in the melt, a thermal gradient caused migration of alkali-bearing magmatic volatiles towards the xenoliths. At the same time the xenoliths were degassed, the effect of both events being a high concentration of volatiles in the host basalt surrounding the xenoliths. The consequent reduction of melting ranges of primary minerals caused resorption of crystals already present in the volatile enriched magma and set up concentration gradients between this and the surrounding basalt. The effect of these gradients was to cause outward migration of elements (mainly Mg and Ca) combined in early-formed minerals of the host rock. Similar concentration gradients existed towards the xenoliths, and reaction products surrounding sandstone xenoliths may be entirely explained by crystallization of diopside and plagioclase within the periphery of xenoliths and additions of MgO to cores of xenoliths. Shale xenoliths, however, have no pyroxene coronas, and there was no significant addition of MgO to cores or margins although pegmatite and trachyte reaction products are well developed. Relatively large losses of SiO₂ from xenoliths have not altered the undersaturated trend of reaction products.

Volatile transport of alkalis began at the time of vesiculation in ordinary basalt, probably contributed to alkali enrichment in reaction products, and continued into the post-consolidation hydrothermal stage. The latter, accompanied by hydrothermal alteration of olivine and plagioclase, probably added to the chemical trends expressed in the primary mineralogy of reaction products.

Some pegmatites are believed to be unrelated to xenoliths, but similar diffusion processes, with volatiles concentrated by shearing along curved flow planes during emplacement, are invoked to explain them.

INTRODUCTION

Peats Ridge, located 50 miles north of Sydney, New South Wales, is an analcite basalt plug, $\frac{1}{2}$ mile in diameter, which is intruded into the Triassic Hawkesbury Formation. Fragments of Hawkesbury sandstone are common in the margin of the intrusion. Also, near contacts, the chilled margin locally contains abundant zeolite amygdules. Large amygdules and some xenoliths exhibit marginal coarse-grained phases, which, though small, afford compact representatives of a wide variety of fabric, mineralogical, and chemical relations found in large pegmatite differentiates of other basic intrusions.

METHODS OF INVESTIGATION

X-ray powder photographs were used for identification of fine-grained secondary minerals and for composition determination of alkali feldspars (Orville, 1958). Olivine compositions were determined from n_z using Kennedy's data (Troeger, 1952), and plagioclase compositions determined with the universal stage (Turner, 1947) using van der Kaaden's data (1951). Pyroxene 2V's all represent direct universal stage measurements in Na light. Rock densities were determined with a Walker balance on specimens which were dried for 24 hours at approximately 100°C.

GENERAL DESCRIPTION

Vertical exposures of about 200 feet are principally restricted to fine-grained, columnar-jointed marginal phases of the intrusion. Columnar joint blocks average 6 to 8 inches in diameter and have a well-developed cross fracture that is not continuous from column to column. Inside the chilled margin, however, cross joints give way to sheet joints that are continuous over considerable distances. Locally, sheet joints pass into the chilled margin as narrow (2 to 3 feet) zones of markedly platy basalt. These show distinct curvature and in places are nearly parallel to columnar joints which themselves exhibit wide divergence of attitude over short distances. A preliminary study of flow structures carried out by T. P. Hopwood has shown that flow lineations are unrelated to either the sheet joints or columnar joints.

Both columnar and sheet joints are coated with green clay, analcite, and natrolite, and sometimes exhibit narrow alteration rinds similar to those described by Smedes and Lang (1955). In places the basalt is intensely altered with formation of abundant green and colorless montmorillonite (see Wilshire, 1958) and natrolite.

Sandstone xenoliths ranging from $\frac{1}{2}$ to 10 inches in diameter are commonly found near the intrusive contacts. The xenoliths show marginal concentrations of zeolite-clay amygdules, abundant interstitial natrolite, and dark glass blebs are sometimes conspicuous. Less common shale xenoliths are also margined by zeolite-clay amygdules. Local concentrations of amygdules occur near contacts, and around the larger amygdules are discontinuous, pod-shaped masses which are coarser grained than ordinary basalt. Although the absolute grain size is not large, these are called pegmatites because they are of restricted size compared with the basalt and are conspicuously coarser grained.

PETROLOGY

Basalt.—The typical basalt consists of glomeroporphyritic aggregates and single anhedral to subhedral grains of unzoned olivine (Fo 74) and microphenocrysts of plagioclase (An 60-68_{core}; An 55_{rim}) set in an intersertal or intergranular groundmass composed of olivine, pale brown clinopyroxene (2V 51°-53°), flow-banded plagioclase and magnetite with or without interstitial brown glass, zeolites, carbonate, biotite, and apatite. Brown spinel with opaque reaction rims, granular olivine aggregates after orthopyroxene, and large olivine grains showing translation lamellae are probably derivatives of peridotite but are rare.

Adjacent to large amygdules there are macroscopically visible alteration halos in the basalt. In most of the halos the only change observable in thin section is complete alteration of olivine (to green trioctahedral montmorillonite, 060 = 1.537A) and plagioclase (to white or green trioctahedral montmorillonite, 060 = 1.536A, analcite, and natrolite); the alteration contact with fresh basalt is very sharp (pl. 1). The outlines of plagioclase crystals are not well preserved, but pyroxene has the same habit and distribution as in adjacent fresh basalt indicating equal volume replacement. There is no apparent correlation between volume of altered basalt and the amount of material in amygdules, and some amygdules have no alteration halos at all.

PLATE 1



Contact between fresh and altered (dark) basalt. The altered basalt is part of a halo surrounding a zeolite amygdale.

Amygdule minerals are dominantly natrolite and analcite but include small amounts of carbonate, unidentified zeolites, white trioctahedral montmorillonite ($060 = 1.523\text{\AA}$), and rarely apophyllite. Carbonate and analcite grains occur typically against cavity walls. Zeolites often fill amygdules completely and clay occurs in the interior of cavities.

Dolerite.—Toward the core of the intrusion basalt gives way to a fine- to medium-grained dolerite consisting of anhedral to subhedral olivine phenocrysts and aggregates set in crudely flow-banded plagioclase laths (An 49-56). Plagioclase is subophitically enclosed in large salite plates ($2V\ 54^\circ\text{--}56^\circ$), which are elongate parallel to the flow banding. Opaque minerals are anhedral or subhedral magnetite and ilmenite. Olivine is partly or completely altered to green clay which is oxidized along minor fractures, and plagioclase adjacent to altered olivine is similarly altered. Accessory apatite is present, along with some interstitial analcite and other anisotropic zeolites.

Sandstone xenoliths.—The abundance of sandstone xenoliths in the chilled margin and their general absence in the coarse-grained interior suggests that most of them were derived from immediately adjacent country rock. The country rock is a dominantly micaceous or argillaceous quartz arenite, which consists of angular to subrounded quartz and quartzite fragments and some biotite in a matrix of finely divided angular quartz and clay (mainly illite with minor kaolinite). Small quantities of detrital leucoxene and feldspar are present.

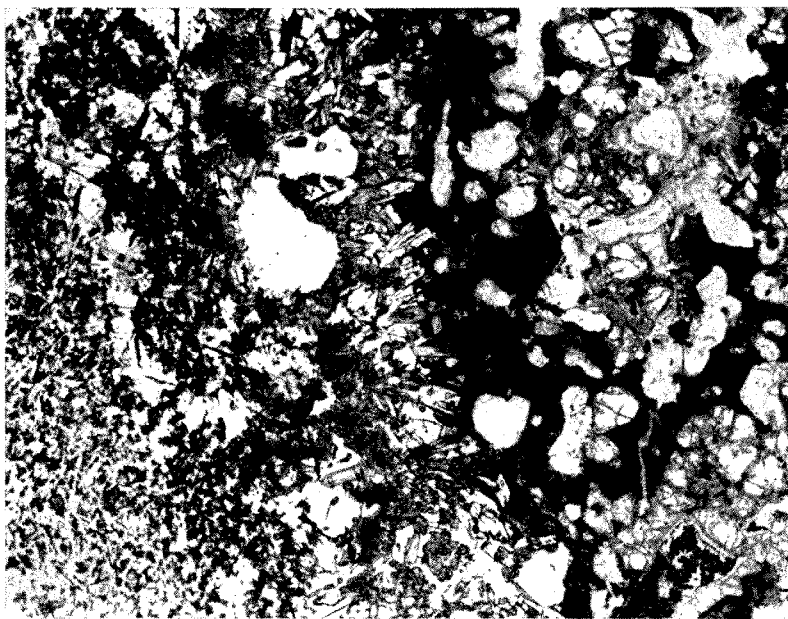
The friable character of the sandstone facilitated disintegration of xenoliths, and many resulting xenocrysts, ranging from 0.1 to 1 mm, are represented in the basalt by characteristic clinopyroxene aggregates. These aggregates typically have an outer rim of fine, granular pyroxene identical with that of adjacent basalt, grading rapidly into a core of much coarser prisms of diopsidic pyroxene ($2V > 56^\circ$) with radial orientation. The larger aggregates (up to 3 mm) contain a little alkali feldspar (?), apatite, magnetite, analcite, and rarely brown glass. Although abundant, none of these aggregates contains any relict quartz, and in all of them clinopyroxene is the dominant constituent. The zoning in granularity and mineralogy is identical with that in reaction rims around large quartzose xenoliths.

The central parts of large sandstone xenoliths exhibit extensive recrystallization and partial fusion. Most of them consist of shattered, resorbed quartz grains with marked undulose extinction set in a turbid matrix of zeolitized glass, scattered magnetite and ilmenite, some turbid, interlocking feldspars, and small quantities of ortho- and clino-pyroxene. Spherulitic zeolite amygdules occur throughout the cores of xenoliths, and carbonate is a common minor constituent in devitrified glass. In some specimens colorless glass ($n = 1.506$) has survived hydrothermal alteration. Near margins of xenoliths colorless skeletal and swallow-tailed diopsidic pyroxenes ($2V\ 52^\circ\text{--}57^\circ$) are scattered through the interstices, and where present in generally colorless glass are surrounded by or enclose deep brown glass. Amygdules consisting of natrolite and cores of colorless triotahedral montmorillonite are common.

Reaction rims around sandstone xenoliths.—The mineralogical and fabric variants in the reaction rims are very complex and are best described by reference to photographs (pls. 2, 3). There is a gradual transition from xenolith margins with a recognizable sandstone fabric to the innermost zone of reaction rims. The most common sequence of zones is that illustrated in plate 2. An inner zone (1) consists of coarse prisms and skeletal crystals of diopsidic pyroxene and plagioclase, and herringbone magnetite clusters set in yellowish to deep brown glass. The glass is usually devitrified to turbid zeolitic material and contains zeolite-clay amygdules. This zone is followed outward by a discontinuous, narrow band of diopsidic pyroxene prisms (2) oriented at a high angle to the xenolith boundary. Towards the basalt this zone gives way abruptly, but with continuous fabric, to a marginal zone (3) in which clusters of small pyroxene granules are scattered through large subhedral to anhedral plates of plagioclase (An 20-22) and alkali feldspar. Proportions of these minerals are extremely variable and no single photograph is representative. There may be some interstitial brown glass enclosing strings of magnetite and plates of ilmenite; apatite is plentiful and zeolite amygdules are fairly common. Fresh and altered olivine grains, usually with stellate clinopyroxene coronas, are scattered through this zone but are far less abundant than in normal basalt.

Another type of reaction rim is illustrated in plate 3. Adjacent to the xenolith boundary is a narrow zone (1) of coarse diopsidic pyroxene prisms in deep brown glass, which grades outward into a zone (2) of deep brown salite prisms and plagioclase laths set in a turbid matrix of devitrified glass and abundant opaque minerals. Zone 2 is similar to an ordinary fine-grained

PLATE 2

*Basalt*

3

2

1

Sandstone

1 mm

Reaction rim around sandstone xenolith. Zone 1: coarse diopsidic pyroxene, plagioclase, opaques, and glass. Zone 2: discontinuous radial pyroxene corona. Zone 3: granular clinopyroxene and opaques in anhedral to subhedral plates of sodic plagioclase and alkali feldspar; scattered olivine grains with clinopyroxene coronas.

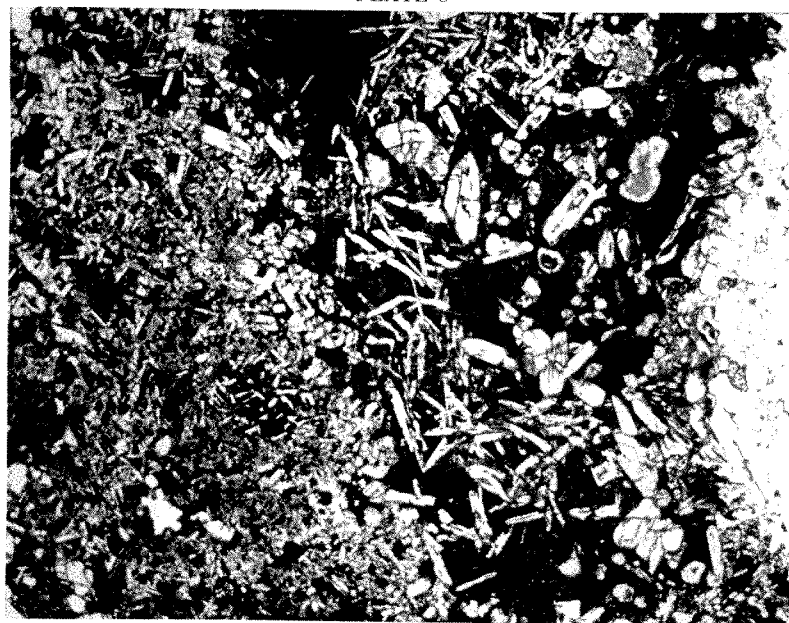
dolerite except for the absence of olivine. This is followed outward by a zone (3) consisting largely of salite with a little plagioclase, brown glass, opaques, and scattered, corroded olivines with salite coronas.

The boundaries of reaction rims either truncate or parallel prominent flow lines in basalt. In some specimens flow structures are locally distorted to conform to the shape of the reaction rim, which itself may have no semblance of a flow structure, but equally commonly flow-banded plagioclase laths project across the reaction rim contact with no change of orientation.

The reaction rims sometimes contain patches or lenses of coarse (up to 3.5 mm) titansalite prisms, plagioclase, small yellowish olivine (?) prisms intergrown at right angles with ilmenite plates, some alkali feldspar, and herringbone magnetite aggregates with or without turbid, finely divided interstitial material. Apatite is generally abundant, and pyroxene is sometimes graphically intergrown with anhedral feldspars or may subophitically enclose plagioclase laths. The fabric is perfectly continuous with that of the surrounding rock. Except for the absence of large olivine prisms, these patches are identical with the pegmatites described in a later section.

One specimen is of special interest in that in hand specimen it appears to be an ordinary natrolite amygdale but in thin section is seen to be sur-

PLATE 3

*Basalt*3 2 1
2 mm

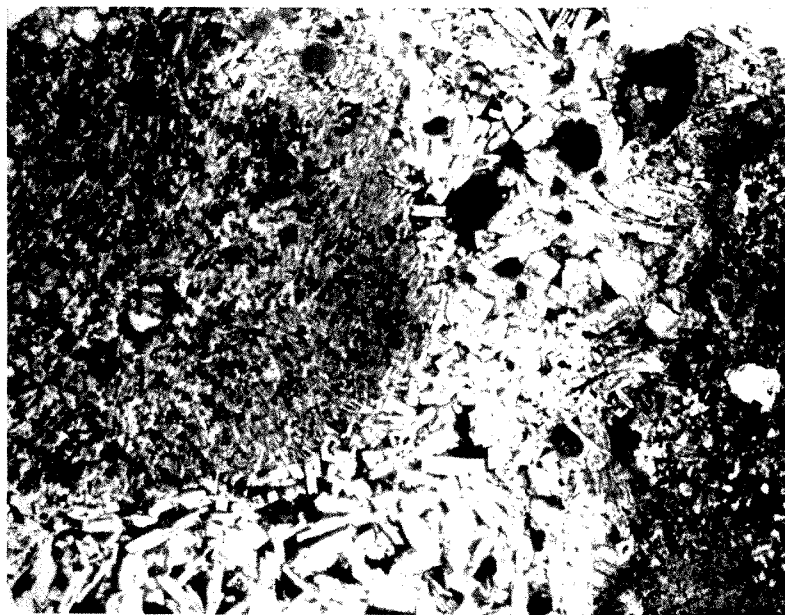
Reaction rim around sandstone xenolith. Zone 1: coarse diopsidic pyroxene in devitrified brown glass. Zone 2: plagioclase laths, titansalite, and opaques in brown glass. Zone 3: dominantly diopsidic pyroxene with some plagioclase, corroded olivine grains with pyroxene coronas, opaques, and glass.

rounded by a rim which is similar to reaction rims around sandstone xenoliths. The "amygdule" has apparently formed by hydrothermal alteration of a sandstone xenolith which, being relatively small, may have been completely fused before metasomatic alteration.

Shale xenoliths.—Cores of shale xenoliths consist of finely bedded angular quartz and clay (mainly kaolinite) and are traversed, usually parallel to bedding, by veinlets of a minutely spherulitic colorless mineral, which may be a zeolite or tridymite. Near xenolith margins spherulites directly replace quartz grains. The cores of most of the larger xenoliths show no trace of anhydrous recrystallization.

Reaction rims around shale xenoliths.—Outer margins of shale xenoliths sometimes grade and sometimes pass abruptly into striking reaction rims which are illustrated in plates 4, 5. Transitional zones (pl. 4, no. 1) consist of turbid material which is possibly zeolitized brown glass, or unaltered colorless ($n = 1.498-1.502$) to brown ($n = 1.518$) glass. Scattered through this are small alkali feldspar (?) crystals, colorless orthopyroxene prisms, minute opaque minerals, and apatite. Natrolite amygdules are common. This passes with continuous fabric outward into a zone (2) of relatively coarse sodic plagioclase and alkali feldspar (Or 18) with interstitial zeolites and zeolite amygdules. Alkali feldspars are often multiply twinned and are triclinic sodic

PLATE 4



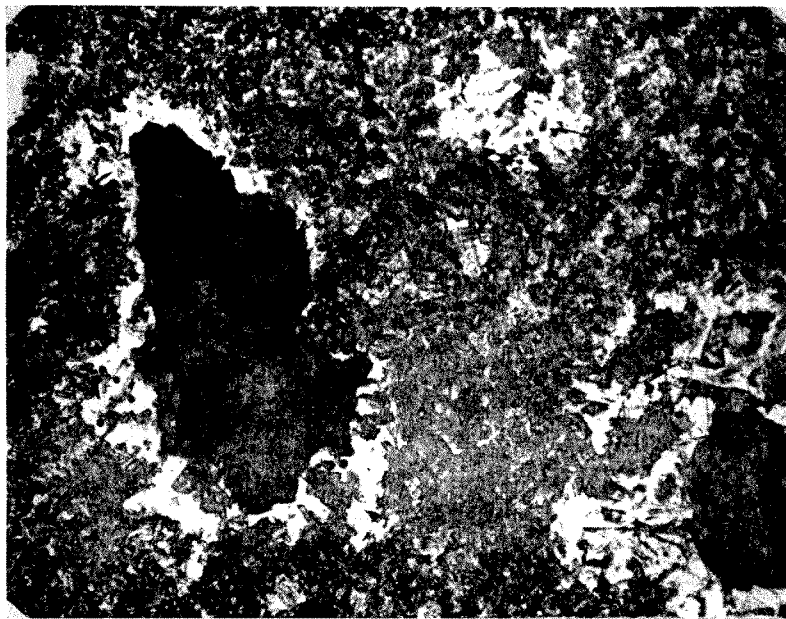
2 1 Shale
 └──────────┘ 1mm

Reaction rim around shale xenolith. Zone 1: turbid transitional zone between shale and reaction rim. Zone 2: coarse alkali feldspar and sodic plagioclase with a little brown glass. Zone 3: flow-banded, fine-grained alkali feldspar and plagioclase laths with variable amounts of granular clinopyroxene, corroded olivine, and opaques.

members of the anorthoclase-sanidine cryptoperthite series (Tuttle, 1952). A very few slender orthopyroxene (?) and clinopyroxene prisms are present. The coarse feldspathic reaction rim passes abruptly, but continuously, into a finer-grained envelope (3), which is locally very feldspathic and contains laths of alkali feldspar and plagioclase flow banded parallel to that in adjacent basalt. Scattered chlorophaeite pseudomorphs after olivine, small opaque minerals, and a very small quantity of colorless clinopyroxene are present. With increasing quantity of colorless pyroxene and diminishing grain size this phase passes gradationally into ordinary basalt. In the outer part of the reaction rims alkali feldspars occur as anhedral, interstitial grains, but plagioclase is still present as flow-banded laths. In some specimens the outer margin of the reaction rim cuts across flow banding, and a few small apophyses project into the basalt. Where these cross flow structures, plagioclase laths always project across the contact. Around some small xenoliths (pl. 5), the coarse feldspathic zone passes directly into basalt.

In one specimen, the coarse feldspathic zone passes rapidly, but with perfect continuity of fabric, into dolerite pegmatite. Although alkali feldspar dominates over plagioclase in the feldspathic zone, the reverse is true in the pegmatite; titanosalite (2V 51°-54°) is much more abundant in the pegmatite, and large prisms of olivine appear that are rare or absent in the feldspathic

PLATE 5



Small shale xenoliths with reaction rims of coarse alkali feldspar and sodic plagioclase. Olivine (altered) grains scattered through reaction rims have diopside pyroxene coronas.

zone. The pegmatite forms a slender extension about 1 inch long into basalt and its lateral contacts with the feldspathic zone of the reaction rim are perfectly continuous (pl. 6). Locally the pegmatite cuts across flow banding in the basalt, but plagioclase laths project for a considerable distance into the pegmatite, and there is even a preservation of plagioclase swirls around olivine in pegmatite adjacent to basalt.

Similar features were observed in the analyzed specimen (table 1, no. 5) in which a shale xenolith is surrounded by a pegmatitic reaction rim up to 1.1 inches wide. No trachyte is present and marginal vitrified shale passes abruptly into the reaction rim. A narrow, fine-grained zone adjacent to the xenolith (pl. 7) apparently represents chilling of basalt against shale, but very few olivine phenocrysts, badly corroded and surrounded by pyroxene coronas, are present. Titansalite of this zone is much more deeply colored than basalt pyroxene, and most of the olivine occurs as minute, yellowish prisms. In the pegmatite large titansalite prisms and plagioclase laths (An 51-52) are set in a turbid matrix of deep brown glass, abundant opaque minerals, and prisms of olivine intergrown with ilmenite. Contacts with basalt are very intricate and many apophyses of pegmatite project into the host rock. These do not disrupt flow structures even where they cross at a high angle, and contacts are generally continuous. Corroded olivine phenocrysts with pyroxene coronas are common near the contacts, both in the pegmatite and in a zone 3 mm wide in the

PLATE 6



————— 1 mm

Outer margin of a reaction rim around a shale xenolith (out of picture, top right). Trachyte, top left, grades laterally into dolerite pegmatite.

host rock. Fabric and pyroxene color variations within the pegmatite are strongly suggestive of recrystallization and replacement of the basalt (pl. 8).

Pegmatites.—Aside from those in reaction rims, seven pegmatites, ranging from 2 to more than 8 inches in maximum dimension, were found. All were located in the chilled margin of the intrusion and all form pod-shaped masses adjacent to natrolite amygdules (pl. 9). The amygdules are surrounded by alteration envelopes in which pegmatite and sometimes basalt are much lighter in color than their unaltered equivalents. Alteration contacts are extremely sharp, but the rock fabric is continuous across them, and intersections of pegmatite and basalt are clearly preserved within the alteration halo (pl. 9). All of the pegmatites have microscopically sharp, but continuous, contacts with basalt and are roughly equidimensional except for the amygdule cavity. Two specimens have intricate, branching apophyses projecting into basalt, but most are smoothly bounded. All pegmatites have a marginal zone of prismatic minerals oriented at a high angle to the contact with basalt in marked contrast to prominent flow banding in the host rock. Inside this relatively narrow zone, pegmatite minerals show no preferred orientation. Some pegmatite margins cut across flow structures (in which case plagioclase laths and sometimes olivine, pyroxene, and magnetite project across the contact), whereas in others there is a local distortion of flow structures to parallelism with pegmatite margins; in places flow-banded plagioclase microlites follow even minor irregularities in the pegmatite contact. Where the associated amygdule is adjacent to basalt

PLATE 7



Dolerite pegmatite reaction rim (left) separated from shale xenolith (right) by a narrow chilled zone.

(pl. 9), flow banding is locally distorted to parallelism with the amygdule boundary. Usually this basalt is in no way different from normal basalt, but one specimen has a distinctly olivine-poor basalt on the opposite side of the amygdule from the pegmatite (right side of amygdule, plate 9; table 1, no. 3). Contacts between this and normal basalt are sharp but continuous.

Principal constituents of the pegmatites are deep purple titansalite ($2V$ 52° - 57°), plagioclase (An 31-52), alkali feldspar, olivine (Fo 57), magnetite, ilmenite, and analcite. Apatite is abundant and minor amounts of biotite and brown amphibole are present. Titansalite occurs as prisms up to 4 mm long, and, in some pegmatites, as graphic intergrowths with feldspar. Near contacts it is often zoned from pale cores to deep purple rims, but deeper in the pegmatite purple cores are rimmed by pale to deep green aegerine augite with magnetite inclusions. Marginal plagioclase usually shows progressive normal zoning with core compositions of An 40-52. Plagioclase from the cores of some pegmatites is more sodic (An 27-35) and may be rimmed with alkali feldspar. Olivine occurs as skeletal prisms up to 4 mm long, and as strings of optically continuous, equant grains. In some pegmatites prismatic olivine is crossed at right angles by ilmenite plates.

INTERPRETATION

Origin of amygdule minerals.—Amygdules, irregularly distributed in the chilled margin and in and around xenoliths, are filled dominantly with natrolite and analcite. These minerals also frequently occur in joints and as minor

PLATE 8



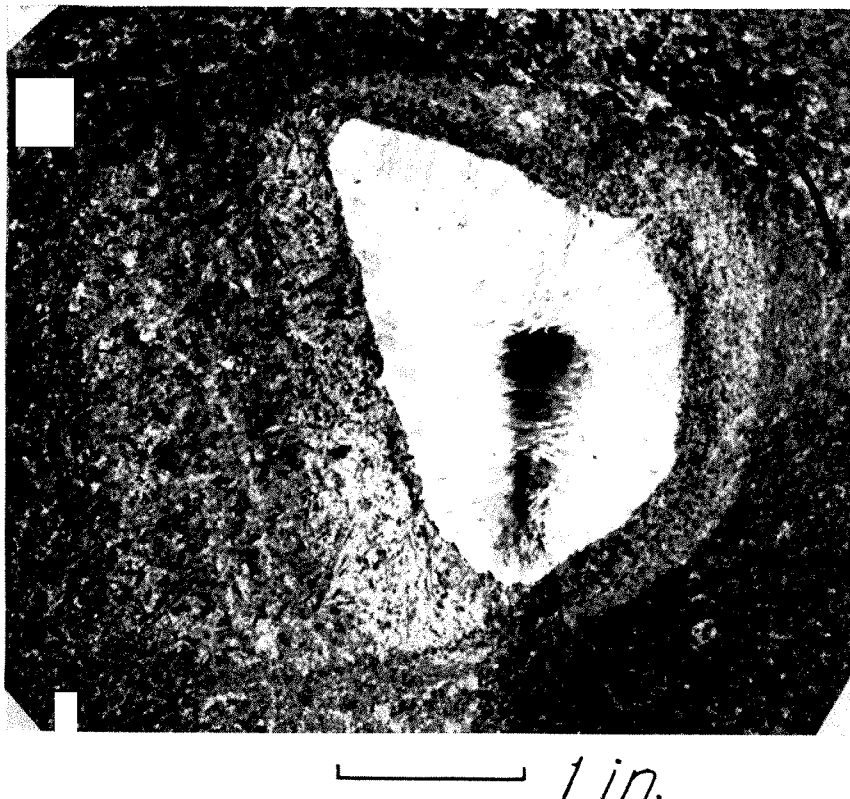
Contact between basalt and dolerite pegmatite which is a reaction rim around a shale xenolith. Note corroded olivine phenocrysts with granular diopsidic pyroxene coronas in the pegmatite.

accessories in the interstices of basalt and dolerite. Ca-rich carbonates, although they occur early in the amygdule paragenetic sequence, are subordinate, and magnesian clays are always late in the sequence and are confined to intensely altered areas. The relation between flow banding and amygdule margins indicates that the cavities formed before complete consolidation and that solution has played at best a very minor part in their formation.

Minerals of the type described here are generally thought to form by low temperature replacement of the host rock by fluids contained in vesicles (Pecora and Fisher, 1946), or by heated water of external (Fenner, 1910), or internal (Williams, Turner, and Gilbert, 1954, p. 23) origin with all constituents other than volatiles leached from the altered host. In a few cases cited by Fenner (1926), formation of anhydrous alkaline minerals in leached xenoliths and fractures is thought to be independent of crystallization or alteration, but Bowen (1928, p. 295) contends that any significant transfer of material by volatiles (without alteration) occurs at a late stage of consolidation and is controlled chemically by fractional crystallization.

The occurrence of alteration rinds along joints suggests an early formation of joints with movement of volatiles towards these low pressure areas, for otherwise a more uniform alteration may be expected. In unaltered basalt analcite and natrolite are the last minerals to crystallize, and if a pressure gradient is set up by jointing (Smedes and Lang, 1955), it seems reasonable to expect a selective migration of late magmatic constituents into low pressure

PLATE 9



Natrolite amygdule with associated dolerite pegmatite (left). Olivine-poor basalt rim on the right side of the amygdule. The outer edge of the light-colored alteration halo bisects the olivine-poor basalt rim, and part of the contact with ordinary basalt is marked in ink. The higher concentration of dark spots adjacent to the amygdule represents altered olivine grains which are nearly three times as abundant as in the olivine-poor basalt.

areas. The amygdule minerals, however, present a different problem, for vesiculation and concentration of at least a gas phase may occur independently of the crystallization history. There seems to be no obvious reason for migration of an alkaline residuum into these cavities; although condensation of vesicle gas may provide room (Pecora and Fisher, 1946), presumably interstitial gas condenses at the same time so that no expansion into cavities would ensue. In addition, concentration of large numbers of amygdules in single joint blocks does not indicate an origin by migration of interstitial fluids, for the basalt, with or without amygdules, contains only a small quantity of interstitial zeolites. Such an origin would probably be completely ruled out if these cavities had to compete with joints for a supply of interstitial residues.

While equal volume replacement of basalt adjacent to amygdules provides a reason for movement of material, the data given in table 1 (Col. A) lend little support to such an origin of natrolite and analcite. Although silica and alumina have been abstracted from the surrounding altered rock, alkalis, par-

ticularly soda, have been lost in negligible quantity. There is, furthermore, no guarantee that losses of silica and alumina are quantitatively adequate to supply the amount of these constituents present in natrolite and analcite, for there is no relation between extent of alteration and size of amygdules, and some amygdules have no alteration halos. Because of this, it is inferred that not only H_2O and minor quantities of other volatiles but also alkalis were separated at the time of vesiculation, and probably independently of the crystallization of anhydrous minerals (Kennedy, 1955). Some silica and alumina may have been concentrated simultaneously.

Reaction rims.—The most striking features of the xenoliths are concentrations in and around them of amygdules, and the more or less sharply defined internal zoning and relatively coarse granularity of the reaction rims. Alkali feldspars are far more abundant and plagioclase less calcic in reaction rims than in basalt, but dense concentrations of pyroxene also occur. The radial pyroxene zone, so common around quartz-rich xenoliths, is absent from reaction rims around shale xenoliths. Small quartz xenocrysts are completely replaced by diopsidic pyroxene, but as the size increases the proportion of felsic constituents in the cores increases.

Petrographically, the various modifications of reaction rims developed around different types of xenoliths correspond to trachyte with or without olivine and pyroxene (shale), dolerite pegmatite (shale and sandstone), olivine-poor, slightly subophitic dolerite (sandstone), phases approaching pyroxenite (sandstone), and those in which variable quantities of pyroxene, usually in clusters, are scattered through platy alkali feldspar and plagioclase (sandstone). No modal quartz is present in any of these modifications and it seems probable that all are undersaturated types toward which the alkali basalt may have differentiated without contamination. While it is sometimes maintained that xenolith composition is the controlling factor in reaction, the author has found only a very few examples in the literature (Holmes, 1936; Reynolds, 1936, 1938) in which reaction between siliceous xenoliths and undersaturated basaltic magma resulted in oversaturated products. Other records (Harvey and Joplin, 1940; Holmes, 1945; Fromm, 1891; Reynolds, 1938; Flett, 1929; Harumoto, 1952) indicate that saturated or undersaturated reaction products often result from reaction of quartz-rich xenoliths with undersaturated hosts. The apparently general belief (Turner and Verhoogen, 1951; Bowen, 1928; Holgate, 1954) that reaction products of siliceous xenoliths and any basaltic magma are of rhyolitic composition, or that such reactions illustrate a mechanism by which the gap between tholeiitic and alkali basaltic differentiation trends may be bridged (Holgate, 1954; Poldervaart, 1948) has no substantial support from occurrences in which xenoliths make up only a small part of the bulk. Evidence from Peats Ridge indicates that, whatever the mechanism was which produced these differentiates which are related to xenoliths, the dominant control is that of the magma and that no divergence from what are widely considered to be the differentiation potentialities of the uncontaminated host has occurred.

The many hypotheses which have been advanced to explain the origin of reaction products differ principally in whether they are treated as products of

replacement of xenoliths, hybridization of the host magma, or partial fusion of xenoliths. Explanations such as simple fusion or partial fusion and withdrawal of appropriate constituents (Bowen, 1928; Daly, 1928; Turner and Verhoogen, 1951) have no application to basic reaction products around siliceous xenoliths and will not be treated further here.

The first question which must be answered to separate the other two hypotheses is whether reaction products represent modified host magma or modified xenolith. Although it is generally impossible to designate the original boundaries of the xenoliths under discussion, there is clear evidence that much of the reaction rim material represents modifications of the host basalt rather than products of replacement of xenoliths. This evidence consists of the occurrence, in all the above-mentioned reaction rim modifications, of corroded olivine phenocrysts which are often surrounded by diopsidic pyroxene coronas, occasional preservation in pegmatite and trachyte modifications of flow lineations continuous with those in adjacent basalt, preservation of feldspar flow swirls around olivine grains, projection of olivine phenocrysts (usually corroded) across boundaries between reaction rims and basalt, and, where "apophyses" of reaction rim material extend into basalt across flow lines, projection of feldspars across the margin without disruption of flow structures. Although flow lineations in the host sometimes parallel even minor irregularities in the contact, the common occurrence of relict olivine within reaction rims clearly points to modification of the host and emphasizes the readiness with which intratelluric phenocrysts may recrystallize with consequent modifications of fabric and mineralogy. Apparent chilling of basalt between the pegmatite reaction rim and shale xenolith (pl. 7) of the analyzed specimen indicates that the entire reaction rim of this specimen represents modified basalt.

If, in the specimens in which it is present, the radial clinopyroxene zone represents the margin of sandstone xenoliths, calcemics have had free entry into peripheral fused xenolithic material as shown by the abundance of coarse pyroxene, plagioclase, and iron oxides within the corona. This conclusion is unequivocally supported by complete replacement of quartz xenocrysts by pyroxene and is opposed to the conclusions of Holgate (1954). Analyses of cores of sandstone xenoliths (table 1, no. 7; Col. B) and of shale xenoliths¹ (table 1, no. 8) also illustrates the addition of aluminous material which is usually present as zeolites. Rarely, aluminous metasomatism has reached the stage of complete replacement of the xenolith by natroite (see above), but more often affected only interstitial glass.

Because of the small size of reaction rims only one analysis (table 1, no. 5) was obtained that represents a pegmatitic modification adjacent to a shale xenolith. However, it is evident from their mineralogy that other modifications

¹ An analysis of shale representing thin lenses in the Hawkesbury Formation was made, but the difference, especially in SiO_2 and Al_2O_3 , between this and the analyzed shale xenolith was so great that they could not have been equivalent. Three other possible sources of the xenoliths are shales of the underlying Narrabeen Formation, the abundant shale lenses at the top of the Hawkesbury, and the overlying Wianamatta shales. The most probable of these is the second named. However, compared with any of these sources, the high-CaO and TiO_2 values in the shale xenolith core and the high alkalis and TiO_2 values in the shale xenolith rim suggest introduction of these constituents.

TABLE 1
Chemical analyses, norms, and modes

	1	2	3	4	5	6	7	8	9	A	B
SiO ₂	45.63	42.07	46.80	46.97	48.50	91.20	70.34	67.74	67.02	-21.3	-30.7
TiO ₂	2.04	2.57	2.61	3.49	3.04	0.84	0.95	1.40	1.70	+1.0	+0.5
Al ₂ O ₃	14.54	11.24	16.93	15.04	15.53	4.81	5.73	14.59	15.30	-12.7	-13.2
Fe ₂ O ₃	1.98	5.08	1.76	2.59	2.90	0.22	1.14	0.25	0.25	+8.1	+2.2
FeO	10.21	7.92	7.99	9.12	8.28	0.08	1.41	1.69	2.10	+3.1	+3.1
MnO	0.19	0.16	0.12	0.16	0.15	nil	0.03	0.05	0.02	-0.1	+0.1
MgO	9.18	8.81	5.32	2.56	4.45	0.03	5.12	0.98	0.83	-5.3	+12.1
CaO	9.83	8.53	10.88	6.62	10.14	0.16	3.08	6.90	3.00	-3.0	+7.0
Na ₂ O	3.46	3.66	3.95	6.54	3.90	0.05	1.41	1.26	2.59	-0.3	+3.2
K ₂ O	1.04	0.32	1.00	2.12	1.05	0.76	1.76	0.52	1.98	-2.2	+2.6
H ₂ O ⁺	1.09	5.12	1.40	2.86	0.95	1.36	3.90	2.01	3.50	+10.8	+6.3
H ₂ O ⁻	0.56	3.77	0.70	0.54	0.48	0.31	3.85	2.14	1.44		
CO ₂	nil	0.21	0.07	0.10	nil	0.23	1.09	nil	nil	+0.6	+2.1
P ₂ O ₅	0.50	0.57	0.54	1.26	0.66	tr	0.13	0.26	0.25	+0.1	+0.3
Total	100.25	100.05	100.07	100.17	100.03	100.05	99.98	99.99	99.98		
S.G.	3.00	2.66	2.83	2.79	2.91	2.16	2.28	2.44	2.68		

	1	3	4	5	C	D	1	3	4	5
or	6.12	6.12	12.23	6.12	2.22	—	—	18.4	5.9	3.4
ab	17.29	22.01	29.34	31.96	9.96	—	—	—	—	7.4
ne	6.53	6.25	14.20	0.57	1.96	11.93	Olivine	30.7	30.6	23.1
lc	—	—	—	—	—	4.80	Clinopyroxene	—	—	—
an	21.13	25.58	5.56	21.96	30.30	19.10	—	—	—	—
di	10.44	10.56	8.35	9.98	11.60	2.09	Feldspar	37.9	52.3	25.0
wo	6.20	6.00	3.50	5.50	6.10	1.30	—	—	—	—
en	3.70	4.09	4.88	4.09	5.15	0.66	Opacues	8.1	8.6	11.4
fs	—	—	—	—	—	—	—	—	—	—
ol	11.76	5.18	2.10	4.06	18.90	32.34	—	—	—	—
fo	7.96	4.08	3.26	3.26	9.18	19.79	—	—	—	—
il	3.95	5.02	6.69	5.78	2.28	0.15	Apatite	tr	0.3	4.4
mt	2.78	2.55	3.71	4.18	2.32	—	Mesostasis	4.9	2.3	37.5
ap	1.01	1.34	3.02	1.68	—	0.34	—	—	—	32.1
Ca ₂ SiO ₄	—	—	—	—	—	6.36	—	—	—	—

Analyst: Mr. J. Pyle, Dept. of Mines, Sydney. 0.04% C in no. 7.

of basaltic composition show much the same chemical variations with respect to the host basalt. These changes consist of increases in the ratios $\text{FeO} + \text{Fe}_2\text{O}_3 / \text{FeO} + \text{Fe}_2\text{O}_3 + \text{MgO}$ and $\text{Fe}_2\text{O}_3 / \text{FeO} + \text{Fe}_2\text{O}_3$ which are taken as guides to stages of differentiation among related basaltic rocks (Walker, 1953). Trachyte reaction rims represent extreme differentiates which may be produced from alkali basalt without contamination. The origin of the reaction rims, then, is a question of how the original basalt was modified mineralogically and chemically and what has produced the differences in fabric.

Upon immersion of xenoliths in the partly crystalline basalt a thermal gradient is set up with a consequent tendency for magmatic volatiles to migrate toward the xenoliths. It was argued in a previous section that alkalis move with the volatiles and that concentration may occur independently of the crystallization of anhydrous minerals. At the same time, the high temperature prevailing in the basalt magma promoted degassing of the xenoliths. The effect of both of these events was a concentration of volatiles in the host basalt adjacent to xenoliths. Any excess volatiles which could not be dissolved by the melt may have formed the vesicles. The consequence of this volatile enrichment was a lowering of melting ranges of the primary minerals so that crystals already present in the melt tended to go back into solution. Subsequent crystallization may then have produced the relatively coarse grained reaction products. Preservation of relict flow structures in marginal parts of reaction rims, however, suggest that direct replacement as well as solution and recrystallization was also involved in forming the new rock types. Because of the presence of glass (sometimes abundant) in most of the reaction products, simultaneous replacement and recrystallization at an advanced stage of crystallization of the host is suggested.

While dilution of the host basalt surrounding xenoliths by magmatic volatiles and their dissolved alkalis may affect the fabric and such ratios as $\text{K}_2\text{O} / \text{K}_2\text{O} + \text{Na}_2\text{O}$ and $\text{K}_2\text{O} + \text{Na}_2\text{O} / \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO}$ of reaction products, such an event will have no influence on the $\text{FeO} + \text{Fe}_2\text{O}_3 / \text{FeO} + \text{Fe}_2\text{O}_3 + \text{MgO}$ ratio of basaltic reaction products nor could it produce trachytic reaction products without concomitant loss of ferromagnesian elements. Relatively large additions of CaO and MgO to the fused peripheries to form diopsidic pyroxene within the radial pyroxene corona (not included in the analysis) may be sufficient to

1. Ordinary basalt, upper chilled margin.
2. Altered equivalent of 1 from an alteration halo surrounding a natrolite amygdale.
3. Olivine-poor basalt near natrolite amygdale illustrated in plate 9; analyzed material excludes that within the alteration halo.
4. Dolerite pegmatite adjacent to natrolite amygdale (plate 9).
5. Dolerite pegmatite in reaction rim around shale xenolith.
6. Unaltered Hawkesbury sandstone 100 yards southeast of quarry.
7. Core of sandstone xenolith, southeast contact zone.
8. Core of shale xenolith, upper south contact zone.
9. Vitified margin of 8.
- A. Changes (gms/cc X 100) in composition of 2 with respect to 1; analyses recalculated to 100% excluding H_2O^- .
- B. Changes (gms/cc X 100) in composition of 7 with respect to 6; analyses recalculated to 100% excluding H_2O^- .
- C. Norm of the most basic material ($\text{H}_2\text{O} = 0$) which can be subtracted from 1 to give 4.
- D. Norm of the most basic material ($\text{Fe}_2\text{O}_3 = 0$) which can be subtracted from 1 to give 5.

account for chemical variations in reaction products around the sandstone xenoliths.

The shale xenoliths and their reaction products are, on the other hand, completely opposed to this interpretation. Trachytic and pegmatitic reaction products are well developed, but there are no pyroxene coronas and no evidence of additions of MgO to either periphery or core of xenoliths. There was probably an addition of CaO to the core of the analyzed xenolith (table 1, no. 8) but this was accompanied by an increase in CaO of the pegmatitic reaction rim (table 1, no. 5) around the same xenolith. In so far as early primary minerals of the host basalt originally surrounding the xenoliths are resorbed by the influx of volatiles, concentration gradients between still liquid phases of reaction rims and the surrounding host basalt may be expected. Crystallization, in the surrounding host rock, of Ca-rich feldspar and pyroxene and Mg-rich olivine may then cause diffusion of appropriate constituents from the reaction rims out into the host. It is possible that dense concentrations of pyroxene at peripheries of some reaction rims represent this outward diffusion of Ca and Mg, but there is little evidence of mafic concentrations around trachyte and dolerite pegmatite reaction rims which are in contact with basalt. At the same time, however, relatively large losses of silica from xenoliths have not altered the undersaturated trend of the differentiates, and perhaps illustrate the effectiveness of diffusion aided by factors discussed by Wahl (1946) and Barth (1952).

The above hypothesis is a modification and elaboration of that set forth by Daly (1912), who suggested that the composition of a hybrid rock surrounding quartzite xenoliths was controlled both by additions (chiefly silica, some alkalis) from the xenolith to the host and by concentrated crystallization of basic hornblendic material between the xenolith and reaction rim. In the present case, analogous crystallization of diopsidic pyroxene adjacent to sandstone xenoliths may have contributed to the relative impoverishment of Ca and Mg in outer zones of reaction rims, but this spatial relationship is not essential as shown by the absence of pyroxene coronas around shale xenoliths. Differences in fabric and changes in composition of the hybrid rock compared with the host, are very similar to the differences between pegmatite and host basalt at Peats Ridge. Whether concentration of calcemics is inside or outside the reaction rim proper, crystallization is, in keeping with Bowen's (1928) assertions, the dominant control. The formation of a liquid that is not intermediate between the host and xenolith by conversion of the xenolith itself to a more basic material (Bowen, 1928, p. 190) does not appear to be adequate, nor can the formation of extreme trachytic differentiates require the same conditions of crystallization as would produce them without contamination (Bowen, 1928, p. 214), if these are viewed in the usual sense as mechanical separation of early-formed crystals from liquid residues. These mechanics have no obvious application to reaction rims which are three-dimensional envelopes around inclusions in fine-grained rocks.

Superimposed on the chemical changes produced by interaction of xenoliths and basalt and those produced by concentration gradients between the reaction rims and host is postconsolidation alkali metasomatism and accom-

panying hydrothermal alteration of primary minerals which produces compositional changes (see table 1, nos. 1-2; Col. A). The combination of all of these events makes it impossible to evaluate quantitatively the contribution of any one of them. The imprint of each, however, is retained in the fabric, primary and secondary-mineralogy.

Pegmatites.—The occurrence of pegmatites in reaction rims around xenoliths may at first sight lend weight to a replacement origin for pegmatites without xenolith cores (Reynolds, 1938; Jones, 1930; Collins, 1925); but, as shown in the previous section, pegmatite reaction rims represent modifications of the magma rather than of xenoliths. Very sharp composition gradients represented by basalt-pegmatite contacts are also opposed to a replacement origin, for the xenoliths are extremely siliceous while pegmatites are undersaturated (table 1). Furthermore, if the type of compositional changes taking place in xenoliths (table 1) continued to the stage of complete replacement, the products would be far removed chemically from the pegmatites. The invariable association of pegmatites with amygdules, combined with the observation that xenoliths can be completely replaced by natrolite (see above), may suggest at least a spatial relation with xenoliths, a relation which Mountain (1943) has shown to be very common. However, the inferred complete replacement of one xenolith by natrolite was based on the presence of a characteristic radial clinopyroxene corona around the amygdule; not one of the large amygdules with pod-shaped pegmatites shows the slightest trace of a reaction rim where it is in contact with normal basalt. At least one, and usually two or more, of the various modifications of reaction rims is present at all contacts of xenoliths with the host, and some evidence of reaction should be present if the amygdules had formed by replacement of xenoliths. For these reasons the large pegmatite patches are believed to be of independent origin. Similar pegmatitic patches with associated amygdules are by no means uncommon (Harvey and Joplin, 1940; Pecora and Fisher, 1946; Walker and Ross, 1954) and are actually large-scale replicas of the very common ocellar structure.

The coarse granularity of basic pegmatites is generally attributed to concentration of volatile constituents (Walker, 1953), an interpretation supported in the present case by close association with amygdules. As shown in the discussion of amygdule minerals, it is likely that alkalis (and possibly other constituents) separate with volatiles and may concentrate independently of the crystallization of anhydrous minerals. Local solution of these constituents in partly crystallized basalt adjacent to large amygdules may then give rise to the same sequence of events outlined in the section on reaction rims: resolution of phenocrysts and diffusion of cations into the surrounding basalt. The cause of local concentration of volatiles in the host may be due to shearing along curved flow planes during emplacement. In this respect, the distortion of flow banding to conform to amygdule boundaries may be due not to continued movement after vesiculation but rather to the separation of a gas bubble in dilatant zones produced by shearing along curved flow planes. This mechanism is similar to that invoked by Brouwer (1936) to explain banding in rhyolite flows, but in the Peats Ridge rocks complicating factors are introduced by disruption of flow structures in the margin of the intrusion. Similar processes may

have influenced the formation of pendant-like pegmatites in reaction rims around xenoliths.

Inasmuch as flow structures are manifest in microlites as well as phenocrysts, movement and deformation at a late stage of consolidation is indicated. Column C, table 1, representing the norm of the most basic material which can be subtracted from the host basalt to produce the analyzed pegmatite, provides a rough idea of the stage of crystallization reached if the diffusion processes outlined above were operative. The high normative plagioclase and pyroxene, compared with the small amount of these present as phenocrysts suggests an advanced stage of crystallization. The same is true of the pegmatite reaction rim (Col. D, table 1), and here there is evidence, in the form of relict basalt fabrics within the pegmatite, that crystallization was well advanced when pegmatites formed. The olivine-poor basalt (table 1, no. 3) was possibly produced by mechanical sorting of olivine phenocrysts during flow as outlined by Wilshire (in press).

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REACTIONS AND MELTING RELATIONS IN THE SYSTEM MUSCOVITE-QUARTZ AT HIGH PRESSURES*

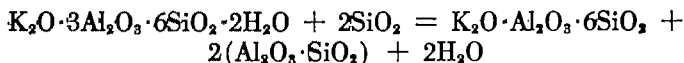
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ABSTRACT. The reaction of muscovite + quartz to sanidine + mullite has been examined as a function of temperature and H₂O pressure to 6 kb. Our results at low pressures are similar to those previously published by Yoder and Eugster. The muscovite = orthoclase + sillimanite isograd, commonly mapped by field petrologists, indicates temperatures in the range 650°-750°C. The reaction muscovite + quartz = muscovite + melt has been determined to 20 kb. The pressure coefficient of melting of a synthetic quaternary granite, where muscovite is the first crystalline phase to form, is approximately 6.5° per kilobar. Thus an ideal granite moving into shallower depths in the Earth's crust from a depth of 30 kilometers can have no more than 16 calories per gram superheat.

INTRODUCTION

One of the commonest metamorphic reactions encountered by the field petrologist is that of the reaction of muscovite + quartz to orthoclase + sillimanite.



Examples of this reaction have been published by many workers in metamorphic terrains, as, for instance, Heald (1950). Both prograde and retrograde reactions have been studied. Muscovite may be converted to orthoclase with increase in temperatures or decrease in pressures of water vapor, and orthoclase may be converted back to muscovite with descending temperatures or increasing water vapor pressures. Knowledge of the position of this reaction boundary allows us to fix maximum temperatures and minimum depths for the genesis of certain groups of rocks. This reaction also provides an upper limit for the freezing temperature of muscovite-bearing granites.

PREVIOUS WORK

Extensive work on the synthesis of micas and their stability range has been published by Yoder and Eugster (1954, 1955; Yoder, 1957).

Yoder and Eugster discuss all earlier experimental studies on the micas, including their synthesis and composition, so a review of prior work is unwarranted here. They studied the reaction of muscovite to sanidine + corundum + vapor up to 2 kb H₂O pressure and 800°C. They have also studied the reaction of muscovite and quartz to orthoclase and sillimanite. Certain problems arose in the interpretation of Yoder and Eugster's results because of the apparent metastable growth of sanidine from mica in the pressure and temperature region believed by them to be in the mica field. It was hoped that new techniques for investigating phase relations at higher pressures and higher temperatures might resolve some of the problems raised by Yoder and Eugster by their work in a lower pressure region.

EXPERIMENTAL METHOD

Two groups of runs were made by us. One group of runs was made in rod bombs at H₂O pressures up to 1000 atmospheres. These bombs are similar

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in operation to the cold seal bombs designed by Tuttle. Samples were sealed in silver tubes approximately $\frac{1}{2}$ inch long and $\frac{1}{8}$ inch diameter and confined within these bombs 15 inches long, 1 inch outside diameter, and $\frac{3}{16}$ inch inside diameter. Pressure was applied by pumping in water. The bombs were heated externally in nichrome wire-wound furnaces whose temperature was regulated by Brown controllers.

Experiments at 6 kb and higher were carried out in piston-anvil apparatus similar to that described by Griggs and Kennedy (1956). A few modifications in the apparatus, as described by Griggs and Kennedy, were made. Chrome carbide pistons, Firth-Sterling grade CR 2, were used. This material is less brittle than tungsten carbide and has resulting longer life at moderate to high pressures. Further, high temperature oxidation of chrome carbide is less severe than that of tungsten carbide. Pistons with vertical sides rather than cone-shaped sides were used, as we have discovered that the support offered by the holder to cone-shaped pistons is not as real as has been initially imagined. A piston and anvil were used rather than two opposing pistons. This minimized the problem of centering the pistons, and the reshaping of the one lower piston was much simplified.

EXPERIMENTAL RESULTS

A number of combinations of starting materials were used in these experiments:

(1) Potassium silicate ($K_2Si_4O_9$), hydrated silica (approximately 16% H_2O), and fused alumina (-300 mesh). Hydrothermal runs with these ingredients showed extremely low reaction rates probably due to the slow rate of solution of alumina in the hydrothermal solution. No reaction whatsoever was observed with these starting materials in the piston-anvil device.

(2) $K_2Si_4O_9$, hydrated silica, and $Al(OH)_3$, gibbsite. The reaction rate of these materials in the hydrothermal apparatus and in the piston-anvil device was also extremely slow. In the hydrothermal apparatus equilibrium was not reached in two weeks at 700°C and 500 bars H_2O pressure. Almost no reaction was observed on runs in the squeezer. At 500°C the gibbsite broke down to corundum, and water was apparently lost from the charge.

(3) Orthoclase, sillimanite, and hydrated silica. Reaction of these ingredients in the hydrothermal apparatus was also slow, and no reaction was obtained in the piston-anvil device, presumably because water could not be held between the pistons with these coarse anhydrous phases.

(4) All the results reported in this paper were obtained using a starting mixture of kaolin and $K_2Si_4O_9$, with and without additional hydrated silica. Mixtures approximately equivalent to 75% muscovite and 25% quartz by weight, kaolin and $K_2Si_4O_9$, as well as mixtures equivalent to 50% muscovite and 50% quartz by weight, kaolin, $K_2Si_4O_9$, and SiO_2 , were prepared.

The products of the runs were identified by the X-ray powder diffraction pattern. This was obtained on a Norelco high angle recording diffractometer using $CuK\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a Ni filter. The majority of the powder patterns were taken at a scanning speed of $1^\circ (2\theta)$ per minute. A quartz plate was used as a sample holder.

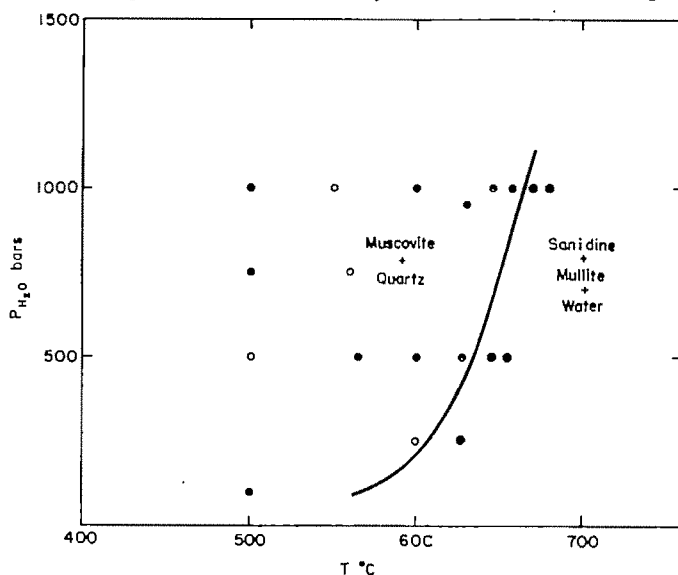


Fig. 1.

Most of the phases from the hydrothermal runs were much too fine grained to be identified under the microscope. These were in marked contrast to the very large flakes of muscovite which grew in many cases in the piston-anvil device. Large single crystals almost the diameter of the piston faces formed in some instances. Results from the hydrothermal runs are shown in table 1 and are plotted in figure 1.

A number of features emerged from the hydrothermal work. Even at temperatures as high as 550°C, equilibrium was not obtained in 18 days. Meta-

TABLE 1
Hydrothermal runs
Starting material, kaolin + $K_2Si_4O_9$ + amorphous silica

T°C	Pressure Bars	Time Days	Phases Identified
500	100	18	Kalsilite, wk. sanidine, wk. muscovite.
600	250	14	Wk. muscovite.
627	250	14	Sanidine, kalsilite, wk. mullite, quartz.
450	500	18	Wk. sanidine, quartz and mullite, tr. muscovite.
500	500	18	Sanidine, quartz, muscovite.
565	500	14	Muscovite, wk. quartz.
600	500	14	Muscovite.
627	500	14	Muscovite, quartz.
645	500	14	Sanidine, mullite, quartz.
655	500	14	Sanidine, mullite, quartz.
500	750	18	Sanidine, quartz, kalsilite, wk. muscovite.
550	750	18	Sanidine, quartz, tr. muscovite.
627	900	14	Muscovite, quartz.
500	1000	18	Muscovite, quartz, sanidine.
550	1000	18	Sanidine, quartz, tr. muscovite.
600	1000	18	Muscovite, quartz.
645	1000	14	Muscovite, quartz.
658	1000	7	Muscovite, quartz.
670	1000	14	Sanidine, mullite, quartz.
680	1000	14	Sanidine, mullite, quartz.

stable sanidine grew very readily at the lowest temperatures. The amount of muscovite present steadily increased at the expense of sanidine up to the limit of the stability field of muscovite where the stable assemblage, sanidine plus mullite, replaces muscovite. These results are in agreement with those of Yoder and Eugster (1955). Yoder and Eugster found the upper limit of stability of muscovite plus quartz to lie somewhere between 650°C and 675°C at 1000 bars H₂O pressure. Our results show the boundary to lie between 658°C and 670°C.

The mixture $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 + 4SiO_2$ was studied in the piston-anvil device. Results from studies of this mixture are shown in table 2 and plotted in figure 2. The reaction of muscovite plus quartz to sanidine plus sillimanite plus water is shown along a dashed boundary. The low temperature-low pressure portion of this boundary is taken from the hydrothermal data shown in

TABLE 2
Runs in piston-anvil device
Kaolin + $K_2Si_4O_9$
($K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 + 4SiO_2 + H_2O$)

T°C	Pressure Kilobars	Time Mins	Phases Identified
695	6	30	Muscovite, quartz.
700	6	30	Muscovite.
725	6	30	Muscovite, quartz.
737	6	30	Muscovite.
750	6	30	Muscovite, tr. sillimanite.
762	6	30	Glass + muscovite.
786	6	30	Wk. sillimanite.
800	6	30	Wk. corundum + glass.
700	8	30	Muscovite, quartz.
725	8	30	Muscovite, wk. quartz.
750	8	30	Muscovite, wk. quartz.
775	8	30	Wk. muscovite.
785	8	30	Glass, wk. muscovite.
805	8	30	Glass, wk. muscovite, wk. sillimanite.
700	10	30	Muscovite, quartz.
722	10	30	Muscovite, quartz.
750	10	30	Muscovite, quartz.
777	10	30	Wk. muscovite.
784	10	60	Muscovite, quartz.
800	10	60	Muscovite, glass.
815	10	60	Tr. muscovite, glass.
825	10	30	Glass.
830	10	30	Glass, wk. corundum (?).
740	15	30	Muscovite, quartz.
800	15	30	Muscovite, wk. quartz.
810	15	60	Muscovite, quartz.
825	15	30	Glass + muscovite.
825	15	60	Muscovite + glass.
855	15	30	Glass, wk. corundum (?).
750	20	30	Muscovite, quartz.
845	20	30	Muscovite, wk. quartz.
850	20	30	Glass + muscovite.
650	30	30	Muscovite, quartz.
700	30	30	Muscovite, quartz.

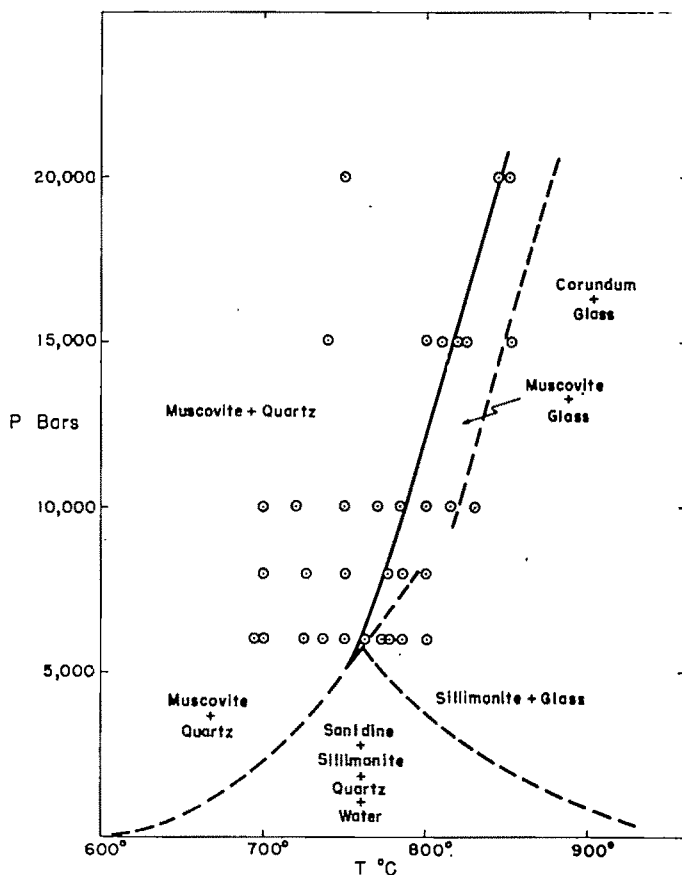


Fig. 2. Reactions with $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 + 4SiO_2$.

figure 1. At low temperatures and low pressures muscovite plus quartz reacts to form sanidine plus mullite. However, there is a continuous solid solution series between mullite and sillimanite, and as pressure and temperature rise, the reaction products of muscovite plus quartz become sanidine plus sillimanite rather than sanidine plus mullite. Details of the sillimanite-mullite solid solution relationship will be published in a forthcoming paper.

The pressures plotted in figure 2 are piston pressures on sample. Along the dehydration boundary, where muscovite plus quartz reacts to sanidine plus sillimanite plus water, the piston pressure is equal to the vapor pressures over the sample. At low pressures and high temperatures sanidine plus sillimanite plus water melts over a temperature interval to sillimanite plus glass. Increasing water pressure, however, lowers the temperature of melting, and at approximately 5 kb the melting curve of sillimanite plus sanidine intersects the muscovite plus quartz stability field. At 6 kb and 760°C muscovite plus quartz melts over an interval to an assemblage of muscovite plus glass plus sillimanite. At 6 kb and 800°C glass plus corundum is the sole product of melting. At 8 kb and above muscovite plus quartz melts to muscovite plus glass. This in turn

melts to glass plus corundum. The details of the intersection of the fields of sillimanite plus glass, muscovite plus glass, and corundum plus glass in the pressure region 5 kb to 8 kb and 750°C to 800°C were not examined and require further study.

The melting curve of muscovite plus quartz was determined to 20 kb, where muscovite plus quartz melts to muscovite plus glass at approximately 845°C. The pressures recorded in figure 2, from 5 kb to 20 kb, are not the H₂O vapor pressures of the system but are the confining pressures on the system. The glass formed by melting contains only the water in the initial muscovite, i.e., for the compositions of these runs, a maximum of 3.6%. Thus the glass is by no means saturated, and unlike the lower portion of the curve where muscovite plus quartz is in equilibrium with orthoclase plus sillimanite plus water, the vapor pressures and confining pressures are not equal. The pressure coefficient for the beginning of melting of muscovite plus quartz is approximately 6½°/kb. This contrasts with the 10°/kb found by Yoder for diopside (Yoder, 1952) and the approximate 12°/kb found by Birch and LaCompte and by Newton, LaMori, and Kennedy (unpublished data) for albite. The low pressure coefficient of melting of muscovite plus quartz is somewhat surprising.

A second group of runs was made in the piston-anvil device. These runs were richer in quartz than the first mixture and of the composition K₂O·

TABLE 3
Runs in piston-anvil device
Kaolin, K₂Si₄O₉, hydrated silica
(K₂O·3Al₂O₃·6SiO₂ + 12SiO₂ + H₂O)

T°C	Pressure Kilobars	Time Mins	Phases Identified
760	6	30	Muscovite, quartz.
780	6	30	Muscovite, quartz, wk. sillimanite.
790	6	30	Glass, wk. sillimanite.
800	6	30	Glass.
760	8	30	Muscovite, quartz.
780	8	30	Muscovite, quartz, wk. sillimanite.
800	8	30	Wk. quartz, wk. sillimanite.
820	8	30	Glass, tr. sillimanite.
760	10	90	Muscovite, quartz.
777	10	150	Muscovite, quartz.
788	10	30	Glass, wk. muscovite, wk. sillimanite, wk. quartz.
796	10	60	Glass, wk. muscovite, wk. sillimanite.
810	10	120	Glass, wk. sillimanite.
800	15	30	Muscovite, quartz.
815	15	30	Muscovite, quartz.
825	15	30	Glass, tr. muscovite, tr. sillimanite.
830	15	90	Glass, sillimanite.
845	15	30	Glass, wk. sillimanite.
855	15	30	Glass, wk. sillimanite.
760	20	30	Muscovite, quartz.
780	20	30	Muscovite, quartz.
790	20	30	Muscovite, quartz.
800	20	30	Muscovite, quartz.
820	20	30	Muscovite, quartz.
835	20	30	Muscovite, quartz.
860	20	30	Glass, wk. sillimanite.

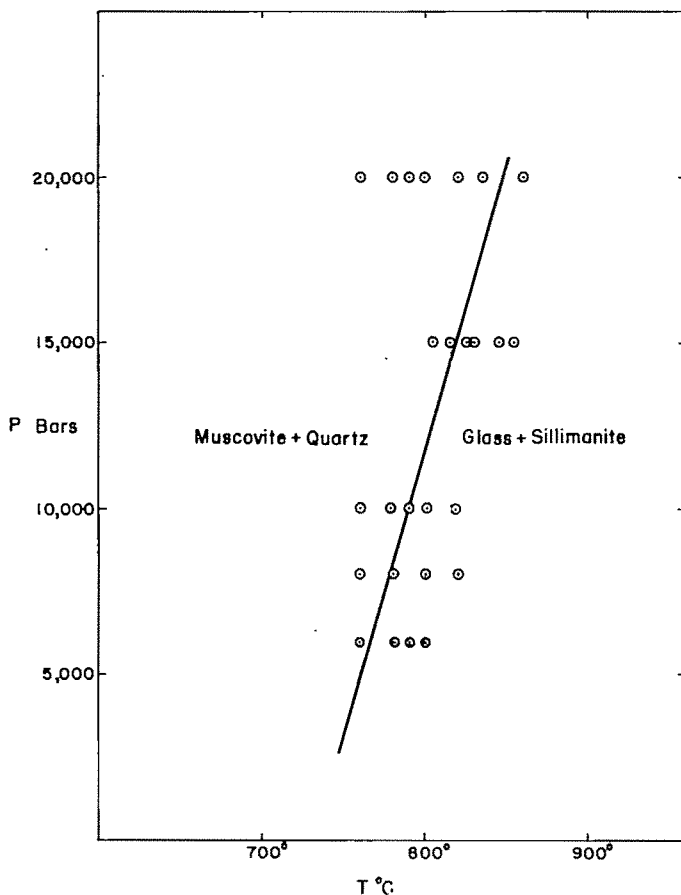


Fig. 3. Reactions with $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 + 12SiO_2$.

$3Al_2O_3 \cdot 6SiO_2 + 12SiO_2 + H_2O$. This mixture of quartz + muscovite is fairly close in composition to an idealized quaternary granite. It contains approximately 71% SiO_2 , 19% Al_2O_3 , 6.5% K_2O , and 3.4% H_2O . The results from runs on this mixture are listed in table 3 and plotted in figure 3. The melting temperature of muscovite plus quartz in this mixture is, as is to be expected, the same as in the previous mixture. However, whereas the first mixtures shown in figure 2 melted to glass plus muscovite, this starting mixture, with the additional quartz present, melts completely to glass plus sillimanite over a very narrow temperature interval. Consequently, the upper limit of the stability of muscovite is some $30^\circ C$ lower in this mixture of higher silica content than in the previously described mixture. The slope of the melting curve, however, is the same, and dp/dt is $6\frac{1}{2}^\circ/kb$.

With the limitation that the quaternary mixture used in this study only approximates the composition of a muscovite-bearing granite magma, the pressure coefficient of melting of a hydrous granite magma can be estimated at $6\frac{1}{2}^\circ/kb$. A granite magma at a depth of 30 kilometers could thus move into

shallow levels in the Earth's crust with approximately 65° superheat. Approximately 16 calories of heat per gram of melt would be available for conversion to kinetic energy and for melting additional materials.

PHASES PRESENT IN THE RUNS

Muscovite.—A single flake of muscovite commonly formed at high pressures in the piston-anvil device. This single crystal gave a biaxial interference figure with optic angle about normal for muscovite. Unfortunately, insufficient material was available from the runs in the piston-anvil device to identify with certainty the polymorphic form of the muscovite. The muscovite formed in the hydrothermal runs at the highest temperature was the 2M polymorph, in agreement with results of Yoder and Eugster (1955).

Sanidine.—Sanidine was not encountered in runs in the piston-anvil device, as melting phenomena intervened before the breakdown of muscovite to sanidine plus sillimanite could be observed. In the low temperature-low pressure hydrothermal runs, sanidine grew readily. This synthetic sanidine gave strong X-ray patterns agreeing closely with those recorded for natural sanidine. No attempt was made to examine the low temperature solidus relations where sanidine should invert, in succession, to orthoclase and to microcline.

Mullite-Sillimanite.—Mullite and sillimanite are part of a solid solution series. Mullite is formed at low pressures and sillimanite forms at higher pressures with a continuum between the two phases. The relations between these two phases have been extensively investigated and will be reported upon in a later publication. No attempt, however, was made to precisely identify the composition of the phase in these runs. Determination of composition by X-ray powder photograph is difficult when only small amounts of these phases are present.

Glass.—The glass observed in the products of the piston-anvil runs had a refractive index of approximately 1.515. The glass is thus within the range to be expected from the compositions involved.

Quartz.—Quartz was not identified optically but was clearly identified in the X-ray diffraction patterns.

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SOME DATA BEARING ON THE ORIGIN OF JAMAICAN BAUXITE

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ABSTRACT. Twenty-nine samples of the White Limestone formation from Kendal, Jamaica, have been analyzed for SiO_2 , Al_2O_3 , and Fe_2O_3 . As the bedrock of the aluminous soils in Jamaica and Hispaniola, the impurity content of this unit has an important bearing on the origin of the bauxite deposits. The average alumina content of the limestone indicated by these analyses is 0.036 percent. This figure corresponds to a tentative value given by Goldich and Bergquist (1948) and confirms their calculation of the thickness of limestone that would have to have been dissolved to account for the present reserves of ore on the Rochelais Plateau in Haiti. The unusual ratios of alumina to silica indicate the presence of excess alumina in the limestone, possibly as aluminum phosphates or alumina hydrates. Efforts at isolating the aluminum-bearing minerals by acid leaching have so far been unsuccessful. The $\text{Al}_2\text{O}_3\text{:Fe}_2\text{O}_3$ ratios of the limestone as determined from these analyses correspond to $\text{Al}_2\text{O}_3\text{:Fe}_2\text{O}_3$ ratios in the bauxite. Such correspondence cannot be taken as evidence that the ores are insoluble residues of the limestone. Both the bauxite and the limestone may have derived their iron oxide and alumina from the older aluminous rocks exposed in the higher central parts of the island.

INTRODUCTION

In a recent reference to the problematic origin of Jamaican bauxite, Eyles (1959, p. 94) suggested that "the only course so far as publication is concerned, is to place on record all the field evidence, and leave others to draw their own conclusions." If this statement may be extended to include laboratory evidence, then the writer is in complete accord and would like to submit some new chemical data that have a bearing on the problem.

At the request of K. K. Landes of this department, the Michigan Limestone Division of the United States Steel Corporation has analyzed twenty-nine samples of the White Limestone formation for SiO_2 , Al_2O_3 , and Fe_2O_3 . The results are presented in table 1. These were samples from the upper 500 feet of core obtained by Alumina-Jamaica Ltd. when they core-drilled a 2000-foot bore in the vicinity of Kendal, Manchester Parish, in 1945.

If the White Limestone is to be considered as one possible source of the bauxite, then it is pertinent to account for the average alumina content, the average Al_2O_3 -to- SiO_2 ratio, and the average Al_2O_3 -to- Fe_2O_3 ratio as indicated by these analyses.

AVERAGE ALUMINA CONTENT

On the assumption that the ores may have come from the limestone, several investigators have attempted to calculate the thickness of limestone that would have to have been dissolved to account for the known reserves of bauxite. In their studies of the aluminous soils in Haiti, Goldich and Bergquist (1948, p. 106) estimated that the formation of the present reserves on the Rochelais Plateau would have required the removal of 1000 feet of the White Limestone over the entire area of the Plateau (a thickness just less than the present relief of that area). Hartman (1955, p. 746) estimated that solution of 800 feet of limestone in the immediate area of the bauxite deposits in the St. Ann District, Jamaica would have released a residue equal in grade and tonnage to the ore reserves in that district. Hill (1955, p. 684) concluded that the

present volume of ore in Jamaica could be obtained by solution of 750 feet of the limestone.

TABLE 1
Chemical analyses of White Limestone samples from the Kendal Core,
Manchester Parish, Jamaica

Core Depth	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Core Depth	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃
100	.12	.01	.25	260	.02	.01	.05
110	.06	.03	.05	270	.02	.01	.07
120	.02	.00	.06	280	.04	.02	.04
130	.06	.01	.03	290	.04	.03	.03
140	.04	.01	.05	300	.04	.01	.01
150	.02	.01	.06	310	.02	.02	.00
160	.02	.01	.11	440	.02	.03	.00
170	.04	.01	.05	450	.04	.03	.00
180	.02	.04	.04	460	.00	.03	.01
190	.02	.04	.02	470	.04	.03	.00
200	.00	.01	.01	480	.00	.03	.00
210	.00	.01	.01	490	.04	.01	.03
220	.02	.04	.00	500	.04	.01	.04
230	.00	.01	.03				
240	.00	.01	.01				
250	.04	.02	.00				

Among the many variables that enter such calculations the average alumina content of the White Limestone is critical. To date, very few analyses of the limestone have been published that give the breakdown of R₂O₃ necessary for a reliable estimate of average Al₂O₃. In their calculations, Goldich and Bergquist assumed an average alumina content of 0.035% but stressed that this number was based on only five analyses of the limestone. Hartman obtained no breakdown of R₂O₃ in his study but, referring to Schmedeman (1948, p. 79), who states that the limestone contains from traces to 0.6% Al₂O₃, he arbitrarily selected a value of 0.075% for his calculations. Hill gave no new Al₂O₃ data but apparently based his thickness estimate on the average weight percentage of insoluble residue in the limestone.

Based on the 29 Kendal Core analyses, the average alumina content¹ of the White Limestone is 0.036±.018%. These data represent only the upper 500 feet of the White Limestone in a single locality, but they do give a quantitatively more reliable idea of how much alumina is available in the bedrock. In calculating required thicknesses of limestone, the end result is inversely proportional to the assumed Al₂O₃ content so that, other factors being equivalent, the difference between .036% and .075% Al₂O₃, say for the St. Ann District, is the difference between 1664 and 800 feet of limestone. Recent estimates place the original thickness of the White Limestone formation at about 3000 feet (L. J. Chubb, personal communication, 1960). Removal of over 1600 feet of limestone would therefore require solution of more than 50 percent of the original volume of the White Limestone Formation. Whether this

¹ The indicated confidence limits are calculated as $\pm t_{.95} s_{\bar{x}} / \sqrt{n}$.

quantity of dissolved limestone can be reconciled with the fact that this rock still covers over one-half the area of the island is a conclusion best left to those working on the problem in Jamaica.

The average alumina content suggested by the Kendal Core analyses is in close agreement with the tentative value published by Goldich and Bergquist (0.035%) and thereby confirms their thickness calculations for the Rochelais Plateau.

Al₂O₃:SiO₂ RATIOS

Dr. Landes first called my attention to the unusual proportions of alumina and silica reported in the Kendal Core analyses. In high alumina clays or other silicates commonly present in marine sediments, the maximum ratio of alumina-to-silica is 0.85 (e.g. kaolinite, ca. .85, montmorillonite .30, illite .33, muscovite .85), but in the White Limestone this ratio averages $1.29 \pm .15\%$.² Looking back to Goldich and Bergquist's published analyses (1948, p. 106), the same high proportions of alumina were noted (table 2).

TABLE 2

Chemical analyses of limestone from aluminous soil localities in Haiti and the Dominican Republic (from Goldich and Bergquist (1948), Norman Davidson, analyst)

Locality	SiO ₂	Al ₂ O ₃
Beaumont, Haiti	.02	.06
Ste.-Croix, Haiti	.02	.01
Savanne Terre Rouge, Haiti	.01	.07
Sierra de Bahoruco, D. Rep.	.05	None
Sierra de Bahoruco, D. Rep.	.03	.03

To judge how unusual such proportions of alumina-to-silica in marine limestones are, the weight percentages of alumina in over 1000 published analyses of limestone were plotted against the corresponding weight percentages of silica in those same limestones. The resulting plot is shown in figure 1. The dashed diagonal line in this graph defines the maximum ratio (0.85) of alumina to silica in high alumina clays. Points falling to the left of this line represent the normal situation in which there is excess silica in the limestone. Points to the right of the line indicate excess alumina which may occur in the rock possibly as alumina hydrates, aluminum phosphates, or as silicates like allophane with unusually high ratios of alumina to silica. This is not to say that these minerals cannot or do not occur in limestones represented by points in the excess silica field. It is just that they must occur in limestones whose analyses place the rock in the excess alumina field.

² The confidence limits indicated here for the ratio Al₂O₃/SiO₂ and for the ratio Al₂O₃/Fe₂O₃ (p. 8) are on a 95% level and are calculated as $\pm t_{.05}(s\bar{x}/\sqrt{n})$. The standard deviation of the ratio of the means ($s\bar{x}/\bar{y}$) is calculated from the following relationship:

$$s\bar{x}/\bar{y} = [\bar{y}^2 s_x^2 + \bar{x}^2 s_y^2 / \bar{y}^4]^{1/2}$$

Circled points representing the Al_2O_3 -to- SiO_2 ratios obtained for the Kendal core samples are also shown in figure 1. A comparison of the White Limestone data with other plotted analyses shows that only 23 of the 1047 published analyses or *two percent* indicate excess alumina, whereas 17 of 29 or *59 percent* of the White Limestone samples contained excess alumina. The proportion of excess alumina in the White Limestone may be greater than these data indicate since uncombined silica is known to occur in the rock as grains of quartz (Hartman, 1955).

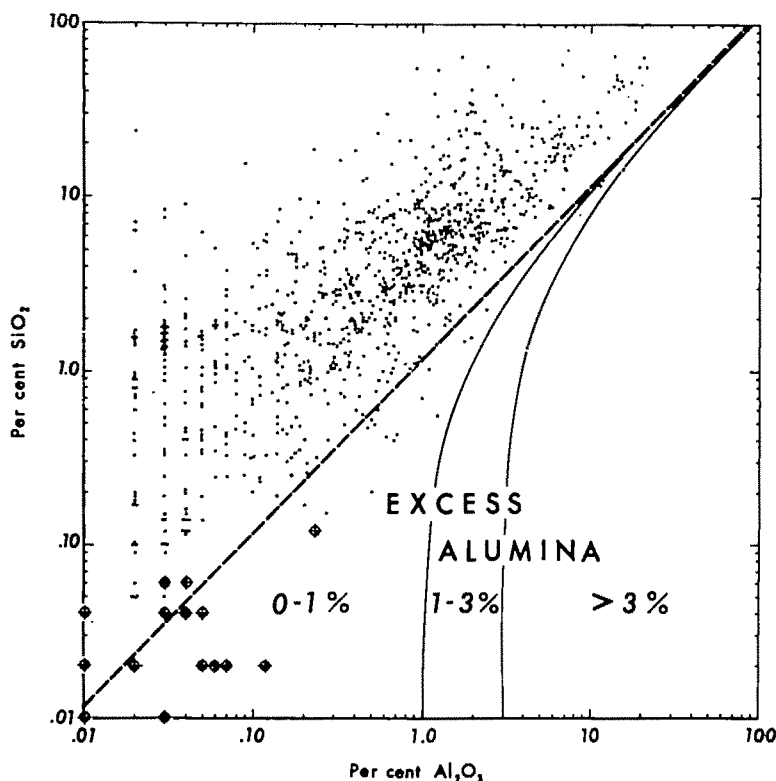


Fig. 1. Alumina vs. silica contents as reported in 1047 published analyses of limestones.

INSOLUBLE RESIDUES OF THE LIMESTONE

Repeated attempts were made to isolate the aluminum-bearing minerals by acid leaching of the limestone, but the results so far are inconclusive.

Residues obtained with dilute hydrochloric acid contained numerous particles of a white to gray, chalky to granular material, several fragments of a transparent to translucent platy mineral, numerous fragments of a greenish yellow transparent mineral, and several small (ca. 1 mm) fish teeth. All of these substances were hand picked and X-rayed, but the only positive identification that could be made was that of the greenish yellow transparent mineral. This gave a definite apatite pattern (table 3) and is presumed to be the same

phosphate as that isolated by Goldich and Bergquist (1948, p. 70) in similar leachings of White Limestone from Haiti.

Leachings with dilute acetic acid released a brown, flocculent substance that remained suspended in the acid bath. This material was centrifuged, washed, and X-rayed (table 3), but again the pattern did not permit any positive identification.

V. A. Zans recently sent the writer two samples of highly phosphatic ore exposed by Alumina Jamaica in one of their pits at Williamsfield. The strong lines in the powder patterns of these materials (table 3) matched those in a standard for pseudowavellite ($3\text{Al}_2\text{O}_3 \cdot 2\text{CaO} \cdot 2\text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$) and confirmed D. J. Burns' previous identification of this mineral (personal communication, V. A. Zans, 1959). Pseudowavellite lines did not appear in the powder patterns of any of the materials in the White Limestone residues.

Additional work along these lines is obviously needed. Once the necessary identifications are made, however, it will be of interest to compare the aluminum mineralogy of the artificial limestone residues with the mineralogy of the phosphorite band locally found between the bauxite and the limestone (Eyles, 1958; Kugler, 1959). Zans' supposition (1959b) that this band represents the true limestone residue is borne out by the presence of apatite and fish teeth in the limestone. Traces of aluminum phosphate minerals have not as yet been identified in the limestone, but their presence or the presence of free aluminum hydroxides is certainly suggested by the alumina/silica ratios in the Kendal Core.

$\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$ RATIOS

The ratio of average Al_2O_3 to average Fe_2O_3 as determined from the Kendal Core analyses is $2.00 \pm 0.21\%$ and thus represents a substantial revision of Goldich and Bergquist's (1948) preliminary estimate of 0.50. Based on bauxite analyses published by Hose (1951, p. 25), the corresponding average of Al_2O_3 -to- Fe_2O_3 for the ores probably ranges from about 2.0 to 2.9.

Similarity in the ratios of Al_2O_3 -to- Fe_2O_3 in the bauxite and in the limestone might be taken as one point in favor of the limestone residue theory. However, this similarity might be expected if both the limestone and the ores derived their iron and aluminum from the older Eocene and Cretaceous rocks exposed in the higher central parts of the island. Bushinsky (1958, p. 176-263; Williams, 1959, p. 95; Zans, 1959a, 1959b) has made this point in reference to similarities in the heavy mineral assemblages of the bauxite and its bedrock, and the same reasoning would seem to apply as well to the sesquioxide contents.

REMARKS

In closing, the writer would like to go on record as supporting Zans' (1959b) recent contention that the Jamaican bauxite is alluvial in origin. Experimentation by Carroll and Starkey (1959) on the leaching of clay minerals in a limestone environment has, in my opinion, demonstrated that the mechanism proposed by Zans is chemically sound. In the light of his observations, the seeming enigma of rich aluminous soils restricted to a bedrock of negligible aluminum content becomes a geologic occurrence consistent with theory.

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REGRESSIONS OF PHYSICAL PROPERTIES ON THE COMPOSITIONS OF CLINOPYROXENES

II. OPTICAL PROPERTIES AND SPECIFIC GRAVITY

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ABSTRACT. New regression coefficients of five physical properties (n_x , n_y , n_z , Z/c , and G) on 15 variables of chemical composition in clinopyroxene [$ABC_2O_6 = (K, Na, Ca, Mn, Fe'', Mg) (Mn, Fe'', Mg, Ti, Fe''', Al) (Fe'', Al, Si)_2O_6$], calculated by least squares from data in 155 selected published descriptions, yield new "best" estimates of the values of these properties for important compositions; the estimates of refractive index are statistically accurate to ± 0.005 or better at the 90% confidence level for all principal "end members" except johannsenite and jadeite, for which data are insufficient, or of insufficient accuracy. The standard deviations decrease as the composition approaches the overall mean composition of the specimens used, reaching an optimum of ± 0.0008 for the refractive indices of the mean.

Best values and standard deviations for some "end members":

	$n_x, \perp b$	n_b	n_z	Z/c	G
Diopside	$1.6658 \pm .0013$	$1.6720 \pm .0014$	$1.6946 \pm .0014$	39.9 ± 0.9	$3.261 \pm .016$
Hedenbergite	$1.7260 \pm .0025$	$1.7318 \pm .0026$	$1.7551 \pm .0027$	42.5 ± 1.7	$3.538 \pm .041$
Clinoenstatite	$1.6503 \pm .0030$	$1.6494 \pm .0031$	$1.6605 \pm .0033$	22.4 ± 1.9	$3.209 \pm .044$
Clinoferrosilite	$1.7691 \pm .0042$	$1.7677 \pm .0043$	$1.8867 \pm .0046$	44.1 ± 2.7	$3.797 \pm .069$
Acmite	$1.7710 \pm .0027$	$1.8103 \pm .0028$	$1.8270 \pm .0030$	104.0 ± 2.0	$3.584 \pm .038$
Jadeite	$1.6560 \pm .0051$	$1.6647 \pm .0053$	$1.6743 \pm .0057$	48.5 ± 6.5	$3.272 \pm .049$

The remarkable success of the regressions in predicting optical properties of clinopyroxenes lends support to the hypothesis of linear, additive variation of these properties throughout the entire clinopyroxene system and thus to the suggestion that the system should be described as a single unit.

I. INTRODUCTION

Graphical methods for dealing with relations between optical properties and chemical composition have been exhaustively used in petrography for many years. The more recent work on the problem by means of multiple regression formulas has had varying degrees of success—and the degree of success seems to be variable in accordance with the viewpoint of the author. Thus Hey (1956), and Winchell and Tilling (1960), who both suggested the use of regressions primarily as a descriptive device, examined their regression constants for significance at a level of confidence corresponding to a risk of about one chance in three or four that a regression constant reported actually should be zero instead of non-zero. Henriques (1958a, b, c) reported regression constants, for some of which the estimated standard errors are larger than the constants themselves. In one report (1958c), the "Student's ratios" are less than unity for more than half of the regression constants calculated! That report seems to prove mainly that second-degree terms (i.e., terms involving x^2) are generally not significant in a descriptive sense even though there may be good theoretical reason to suppose that their coefficients should differ from zero. Part of the difficulty was the limited range of values for most of the composition variables.

Using a more interpretative approach, both Hori (1954) and Henriques (1958a, b, c) attempted to isolate the effects of the individual constituent cations on the optical properties. This approach may be justified, but both of

these authors based their results on the same limited range of compositions just mentioned.

In Part I of this series (Winchell and Tilling, 1960) was presented a somewhat oversimplified study of the regressions of lattice constants of clino-pyroxene on chemical composition. That study had to be based upon uncomfortably few specimens, and especially few containing major amounts of sodium in the A-position of the formula ABC_2O_6 . In the present study, one is more likely to be embarrassed by the abundance of published data than by its scarcity: this embarrassment of riches presents no difficulties in calculations, however, when a speedy digital computer is used. Its main embarrassment is the necessity of presenting rather long tables of data and residuals (tables 2, 3).

2. ACKNOWLEDGMENTS

Several members of the Yale advanced mineralogy class in 1958-1959 contributed significant aid in collecting and checking data. Many of the analyses from the literature were originally assembled by A. N. Winchell in a file of information on the chemistry and optics of minerals that he turned over to me about six years ago. To the Higgins Trust Fund of Yale University, and the Yale University Computing Center I am grateful for financial assistance that permitted the calculations to be done at the Center. The one-pass least squares regression routine used was written by Harold Watts for the IBM 650 digital computer. To Dr. Michael Fleischer of the U. S. Geological Survey are due my thanks for important bibliographic aid.

3. REGRESSION THEORY; DEFINITIONS OF VARIABLES

General linear multiple regression formulas are well known, as are the methods for their solution by least squares procedures. Davies (1958), Fisher (1958), and many others outline these theories and illustrate them by more or less easily understandable examples. Acton (1959) gives a clear description of some of the basic concepts of regressions limited to two dimensions only. Regression theory and its mineralogical applications were reviewed by Hey (1956) and, briefly, in the first paper of this series (Winchell and Tilling, 1960). Regression equations resulting from the calculations may be collectively represented as follows:

$$y'_p = (b_0 \pm s_{0p}) + \sum (b_{ip} \pm s_{ip}) x_i \pm s_p. \quad (1)$$

Here y_p is used to represent five different dependent variables (refractive indices n_x , n_y , n_z , extinction angle Z/c , and specific gravity G , for $p = 1, 2, \dots, 5$, respectively); it is written y if observed, and y' if estimated by equation 1, and the mean value is $\bar{y}$. The several variables x_i ($i = 1$ to 12, and even 0 for a "pseudo-variable" equal to unity) represent the chemical components that are treated as independent variables. The estimated multiple-regression constants are b_{ip} , each with its standard error s_{ip} ; the standard error of regression is s_p , defined by equation (2), where E_{np} is the residual, $y_p - y'_p$ for the n^{th} observation, and F is the number of degrees of freedom, $N - 12 - 1$, among the N observations used for estimating 12 regression constants b_{ip} , and b_{0p} .

$$s_p = \sum E_{np}^2 / F. \quad (2)$$

There are at least 15 different constituents in clinopyroxene. Ten different elements, Si, Al, Fe^{'''}, Ti, Mg, Fe^{''}, Mn, Ca, Na, and K are commonly reported as oxides in chemical analyses, but several of these may enter the structure of the crystalline mineral in distinct positions and may be expected to have correspondingly different effects upon the physical properties. The formula is written ABC₂O₆, and the chemical analyses recast accordingly to a total of exactly six (or 6000) oxygens. The cations are then assigned in the order of increasing ionic radius to fill the positions C and B, the remainder being considered as A. We thus obtain a total of 15 chemical variables x_1 and z_j by the scheme shown in table 1. The summations of anions to six, cations C to two, and cations B to one are exact; cations A ought to total one, but in fact rarely do. However, a third exact linear relation among the cations is determined by the total cation valency of 12 to balance the charge of the six oxygens. Therefore three of the composition-variables (z_j in table 1) can be selected and designated as dependent upon the others. The z_j in table 1 were selected so that a common end member, diopside, lies at the origin of coordinates where all the x_1 -values are zero. The final regression equations therefore contain as constant terms b_{op} the properties of diopside.

TABLE 1

Definitions of variables x_1 , y_p , and z_j , and an example of their calculation from analysis 155, clinopyroxene from layered basic rocks of Rhum (Brown, 1956).

Physical properties: $y_1 = n_x = 1.6820$, $y_2 = n_y = 1.6870$, $y_3 = n_z = 1.7092$, $y_4 = Z/c = (?)$, $y_5 = G = 3.33$. Formula type ABC ₂ O ₆ .						
Chemical data:						
	% wt.	Rel. No. Anions	No. Cations to 6000 Anions	Cations C	Cations B	Cations A
SiO ₂	51.90	17282	1902	$z_1 = 1902$		
Al ₂ O ₃	3.40	1000	147	$x_1 = 98$	$x_2 = 49$	
Fe ₂ O ₃	0.53	99	15	$x_2 = 0$	$x_4 = 41$	
Cr ₂ O ₃	0.88	174	26			
TiO ₂	0.46	116	13		$x_5 = 13$	
MgO	17.00	4216	928		$z_2 = 897$	$x_3 = 31$
FeO	3.70	515	113			
NiO	n.d.	—	—		$x_6 = 0$	$x_8 = 113$
MnO	0.12	17	4		$x_7 = 0$	$x_{10} = 4$
CaO	21.12	3766	830			$z_3 = 830$
Na ₂ O	0.36	58	26			$x_{11} = 26$
K ₂ O	0.03	3	1			$x_{12} = 1$
H ₂ O	0.25	—	—			
	99.75	27246	4005	2000	1000	1005

Note: The z_j 's depend upon the x 's as follows:

$z_1 = 2000 - x_1 - x_2 - x_5$ —as determined by space availability

$z_2 = 1000 - x_3 - x_4 - x_6 - x_7 - x_8$ —as determined by space availability

$z_3 = \frac{1}{3}[2000 + x_1 + x_2 - x_3 - x_4 - 2x_5 - 2x_6 - 2x_7 - x_{10} - x_{11} - x_{12}]$ —as determined by valency balance with small errors possible due to incorrect ($\neq 4000$) sum of cations.

A perfectly ordered distribution of the cations is implicit in the calculation of analyses and definition of composition-variables. This oversimplification clearly needs further study, although there is some justification for it in the precise X-ray structural work of Ghose (1960) who showed practically perfect ordering of Fe²⁺ and Mg in positions corresponding to A and B, in an orthopyroxene from a metamorphic rock, and in the work of Morimoto, Appleman, and Evans (1959, table 25), who found all Mg in B, all Ca in A, and Fe²⁺ distributed between A and B as required by the composition, in a ferropigeonite from a dike rock near Asio Mine, Japan. Although the hypothesis of perfectly ordered distribution of the elements is thus strengthened by two examples of low-calcium pyroxene, variations in the degree of order are nevertheless to be expected, and should be tested.

Table 1 shows definitions of variables x_1 , y_p , and z_j and illustrates the calculation of the x 's and z 's for a single analysis. Any analysis, for which (with oxygens = six) the sum of all the cations differs by more than 0.030 from exactly four, was automatically subject to suspicion and normally rejected. Exceptions to this rule were made for specimens with unusual composition if good determinations of physical properties were available. Cr₂O₃ and NiO are occasionally given in analyses; these components were combined with Fe₂O₃ and FeO, respectively, to homogenize the data for computation. Hori (1954) calculated almost equal regression constants for Fe²⁺ and Cr, lending some justification for one of these combinations. Neither Ni nor Cr is present in large amount, and these elements are reported in only a small fraction of the analyses anyway. Also for arithmetical convenience, the alkalis K₂O and Na₂O were considered zero in about a dozen analyses of diopsidic material for which they were not reported; better wisdom might suggest using average values, but alkalis are rarely omitted from determination in specimens where they are likely to be present in significant amounts; mean values for analyses not reporting them would therefore tend to be closer to zero than the means for all analyses, for the latter include the analyses of acmite, aegirite, and jadeite.

4. SELECTION OF ANALYSES: PHYSICAL PROPERTIES

Several hundred analyses of clinopyroxene have been published with correlated physical data. Unfortunately, many reports are incomplete or of limited accuracy in various ways. Those for which refractive indices are uncertain by as much as 0.010 were ordinarily rejected. Most index determinations accepted are probably accurate to 0.003 or better. In cases where two refractive indices are given, the third index can be estimated with adequate accuracy if 2V is known to the nearest 5°, and probably even if it is known to the nearest 10°. No regression study was attempted for 2V because its relation to indices is inherently non-linear, though in fact several regression studies (Hori, 1954; Henriques, 1958b, c) and numerous well-known graphical presentations either demonstrate or imply at least approximate linearity of 2V with composition parameters.

Optic orientation is expressed by the two items, Y (or X) = b , and the extinction angle Z/c . The change from $Y = b$ to $X = b$ is accompanied by the crossing of curves for n_b and n_1 , where n_1 is the smaller principal refrac-

tive index in the plane of the axes a and c , and n_b is the index for light vibrating parallel to b . This condition occurs in low-calcium pigeonites. Specimens in which it occurs may be identified in table 3 by the fact that their refractive indices in the column headed y_1 (n_x) are larger than those in the column headed y_2 (n_y). Extinction angle is measured in the obtuse angle between c and a ; there is usually no uncertainty in the value or the sign of this angle, but in a few cases the published descriptions give X/c instead of Z/c , and fail to show whether X lies in the obtuse or the acute angle between c and a . If X/c is designated positive when X lies in the obtuse angle, then $Z/c = 90^\circ + X/c$. Washington and Merwin clearly indicated the sign of the measured extinction angle X/c in their descriptions of specimens 086-090 (tables 2, 3). In most cases there is no doubt anyway, because Z/c is greater than 90° only for compositions containing more than about 85% acmite (for which $2V_x > 110^\circ$, and $n_y > 1.787$; Winchell and Winchell, 1951, p. 415-416). Ambiguity is therefore a serious risk only for specimens with this limiting composition and its associated properties.

The values of Z/c and of the specific gravity G are frequently omitted from published descriptions of analyzed specimens. This made it necessary to compute separately the regressions for these properties even though the extinction angle actually varies so slightly from 43 to 44 degrees in diopsidic and augitic specimens that it might safely have been supplied for most of them to gain computational convenience.

Table 2 shows the compositional data for 155 selected clinopyroxene specimens. The quantities designated x_i are treated as the independent variables for calculating the regressions; those designated z_j are additional chemical variables that are constrained by the formula ABC_2O_6 and by considerations of valency, as shown in table 1. The analyses include representatives of all significant compositions found among clinopyroxenes, although the number of jadeites, and of intermediate specimens in the subsystem jadeite-acmite-salite could well be increased. If we strike from the list every analysis containing at least one composition-variable (x_i or z_j) that is within the group of the ten analyses having the highest values for that variable, there remain about 70 analyses that are "intermediate" in all respects. These include many augite and diopside specimens but are widely enough distributed to warrant the conclusion that the table represents the clinopyroxene system as a whole, and that there are no really large gaps in the data.

The observed physical properties for the same specimens are listed in the columns headed y_p in table 3, together with the residuals $E_p = y_p - y_p'$ representing the differences between observed values of these properties, and those calculated by means of equation (1), using the regression constants b_{ip} shown in table 4. Table 3 shows that the refractive indices have been predicted from the compositions with an accuracy in the neighborhood of $\pm .005$, the extinction angles to $\pm 4^\circ$, and specific gravities to $\pm .05$. These figures are comparable to the accuracy of the original data; they are approximately the standard errors of regression, s_p . Specimens with residuals greater than about 2.5 times s_p are immediately suspect because the probability of such deviations (Text continued on page 305.)

TABLE 2. CLINOPYROXENE ANALYSES RECAST AS ATOMS OF METAL PER 6000 OXYGEN ATOMS

NO.	POSITION C			POSITION B							POSITION A					
	SI	AL	FE3	AL	FE3	TI	MG	FE2	MN		MG	FE2	MN	CA	NA	K
	*21	X1	X2	X3	X4	X5	*22	X6	X7		X8	X9	X10	*23	X11	X12
001	1856	144	000	129	080	025	0703	063	000		000	207	007	0710	028	002
002	1836	164	000	030	043	017	0910	000	000		280	301	009	0435	013	000
003	1868	132	000	023	054	024	0875	024	000		000	239	006	0732	050	000
004	1862	138	000	083	039	033	0714	131	000		000	238	005	0721	041	006
005	1911	089	000	032	018	033	0759	158	000		000	040	007	0877	044	013
006	1822	178	000	027	007	032	0705	236	000		000	072	010	0837	038	007
007	1795	205	000	002	014	030	0703	251	000		000	067	012	0964	041	005
008	1840	160	000	031	068	025	0776	100	000		000	211	008	0777	027	009
009	1889	086	025	000	059	051	0645	265	000		000	293	004	0649	036	014
010	1833	167	000	060	023	054	0668	195	000		000	371	012	0583	033	007
011	1916	042	042	000	020	031	0639	310	000		000	285	009	0685	046	004
012	1698	302	000	057	201	010	0701	013	005		000	000	000	1015	024	018
013	1905	095	000	011	042	021	0618	308	000		000	252	007	0694	029	004
014	1920	037	043	000	046	026	0604	324	003		000	249	010	0703	037	004
015	1886	074	040	000	009	037	0520	434	000		000	238	012	0736	030	007
016	1881	119	000	000	086	033	0376	305	000		000	207	014	0717	043	014
017	1850	150	000	042	036	047	0271	604	000		000	200	014	0747	041	011
018	1918	082	000	011	039	036	0155	759	000		000	167	007	0773	049	015
019	1942	058	000	023	058	010	0783	126	000		000	083	049	0899	028	004
020	1867	133	000	145	057	037	0048	713	000		000	114	025	0761	048	008
021	1955	045	000	066	062	022	0049	801	000		000	215	041	0698	063	011
022	1925	075	000	045	045	025	0042	843	000		000	187	035	0709	055	010
023	1785	215	000	043	118	053	0029	757	000		000	348	028	0550	083	012
024	1956	018	026	000	005	007	0988	000	000		317	522	018	0160	013	000
025	1851	149	000	065	022	011	0827	075	000		000	108	000	0903	013	000
026	1883	117	000	011	013	013	0784	179	000		000	052	002	0946	022	004
027	1911	089	000	005	027	022	0917	029	000		000	179	007	0794	022	009
028	1906	094	000	019	018	007	0956	000	000		023	425	014	0574	000	000
029	1896	037	067	000	029	018	0927	026	000		000	553	018	0405	050	009
030	1903	028	069	000	037	021	0942	000	000		001	576	025	0392	028	005
031	1958	000	042	000	005	009	0747	239	000		000	520	009	0467	024	009
032	1866	134	000	045	053	015	0869	000	000		071	097	000	0805	027	013
033	1930	033	037	000	076	019	0905	000	000		004	760	080	0132	000	000
034	1965	035	000	008	052	026	0751	163	000		000	752	033	0161	019	005
035	1971	029	000	025	060	001	0906	000	000		010	028	003	0921	016	004
036	1953	047	000	040	047	006	0907	000	000		028	076	002	0855	026	000
037	1891	109	000	048	052	004	0896	000	000		094	109	004	0784	011	004
038	1889	111	000	017	068	008	0907	000	000		187	130	004	0704	020	000
039	1912	088	000	039	066	007	0888	000	000		099	122	004	0752	022	000
040	1931	069	000	049	048	013	0890	000	000		003	173	004	0781	024	000
041	1884	116	000	049	060	027	0864	000	000		023	169	007	0752	049	002
042	1934	066	000	051	038	012	0875	024	000		000	155	006	0808	020	000
043	1935	065	000	037	042	013	0864	044	000		000	161	007	0800	022	000
044	1918	082	000	051	038	013	0883	015	000		000	207	006	0762	020	000
045	1935	065	000	043	045	016	0808	088	000		000	206	008	0758	013	000
046	1927	073	000	038	036	011	0793	125	000		000	240	010	0728	022	000
047	1920	080	000	039	053	011	0697	200	000		000	117	016	0830	034	000
048	1937	065	000	061	069	007	0550	313	000		000	097	005	0828	055	005
049	1979	021	000	047	078	006	0510	359	000		000	063	028	0830	090	000
050	1990	010	000	040	014	002	0334	610	000		000	000	006	0962	014	000
051	1958	042	000	064	055	008	0410	463	000		000	131	028	0767	047	003
052	1988	012	000	003	047	002	0064	788	096		000	000	003	0938	012	000
053	1977	023	000	046	123	009	0020	802	000		000	123	026	0710	121	007
054	1964	036	000	047	130	002	0636	185	000		000	065	007	0815	118	000
055	1890	110	000	081	056	019	0676	168	000		000	112	007	0827	039	000
056	1892	108	000	101	076	016	0617	190	000		000	113	007	0791	061	007
057	1870	130	000	067	061	021	0502	349	000		000	068	007	0891	039	000
058	1775	225	000	097	091	042	0486	284	000		000	049	007	0896	051	000
059	1755	245	000	109	098	037	0407	349	000		000	049	005	0892	045	009
060	1823	177	000	033	085	043	0408	411	000		000	033	007	0913	035	000
061	1948	052	000	003	079	011	0203	704	000		000	120	021	0818	037	010
062	1912	088	000	064	045	029	0812	050	000		000	243	008	0740	027	000
063	1900	100	000	026	040	028	0793	113	000		000	206	008	0765	022	000
064	1903	097	000	020	035	029	0785	131	000		000	193	008	0772	022	000
065	1914	086	000	023	027	029	0758	163	000		000	210	009	0760	020	000
066	1916	084	000	059	020	014	0756	151	000		000	262	010	0703	020	002
067	1918	082	000	030	017	025	0739	189	000		000	262	013	0707	018	000
068	1939	065	000	036	024	024	0718	198	000		000	323	010	0632	020	000
069	1986	014	000	003	011	001	0932	053	000		000	019	005	0971	004	002
070	1965	035	000	026	009	001	0906	058	000		000	021	007	0966	010	001
071	1895	105	000	012	086	007	0693	202	000		000	033	014	0949	033	000
072	1880	120	000	059	111	008	0509	313	000		000	024	013	0955	038	000
073	1793	207	000	028	174	009	0403	386	000		000	011	014	0945	026	000
074	1920	042	038	000	162	006	0649	183	000		000	037	000	0847	136	002
075	1964	036	000	037	005	015	0993	000	000		000	744	016	0183	007	000
076	1986	014	000	035	002	014	0856	093	000		000	777	019	0179	002	000
077	1945	055	000	016	021	005	0912	046	000		000	794	012	0194	000	000
078	2000	000	000	000	000	000	1000	000	000		999	000	000	0000	000	000
079	1962	011	027	000	018	000	0921	061	000		000	018	006	0980	011	000
080	1906	094	000	081	672	023	0132	092	000		000	003	065	0278	556	039

NO.	POSITION C			POSITION B							POSITION A					
	SI	AL	FE3	AL	FE3	TI	MG	FE2	MN		MG	FE2	MN	CA	NA	K
	*Z1	X1	X2	X3	X4	X5	*Z2	X6	X7		X8	X9	X10	*Z3	X11	X12
081	1874	122	004	000	078	018	0753	151	000		000	084	016	0899	045	000
082	1950	050	000	050	027	009	0639	275	000		000	017	015	0923	030	005
083	1848	152	000	073	052	011	0848	016	000		000	085	004	0899	031	000
084	1906	071	023	000	043	028	0550	379	000		000	229	014	0735	019	000
085	1873	127	000	245	450	031	0274	000	000		041	069	025	0220	666	014
086	2001	000	000	044	918	018	0014	006	000		000	007	012	0023	874	018
087	1967	033	000	063	854	030	0021	032	000		000	019	005	0013	972	010
088	1968	032	000	048	833	007	0020	092	000		000	007	010	0054	946	018
089	1997	003	000	057	839	016	0025	063	000		000	007	003	0070	868	012
090	1957	043	000	039	684	003	0086	170	003		000	000	000	0246	739	012
091	1922	066	012	000	076	010	0785	129	000		000	073	017	0858	027	000
092	1898	102	000	029	066	027	0793	085	000		000	229	005	0716	049	000
093	1913	087	000	105	345	023	0220	307	000		000	009	013	0548	405	020
094	1994	006	000	048	613	072	0221	046	000		000	504	014	0207	744	009
095	1942	058	000	044	407	012	0305	232	000		000	308	020	0853	398	019
096	1444	556	000	094	133	166	0388	219	000		000	010	005	0993	007	000
097	2000	000	000	000	000	000	1000	000	000		000	000	000	1000	000	000
098	2000	000	000	000	000	000	1000	000	000		466	000	000	0534	000	000
099	2000	000	000	000	000	000	1000	000	000		655	000	000	0345	000	000
100	2000	000	000	000	000	000	1000	000	000		826	000	000	0174	000	000
101	2000	000	000	000	000	000	1000	000	000		999	000	000	0000	000	000
102	2000	000	000	000	000	000	1000	000	000		000	000	000	1000	000	000
103	1949	051	000	028	056	002	0246	623	045		000	000	045	0934	000	000
104	1993	007	000	033	034	004	0133	384	412		000	000	075	0900	008	001
105	1992	008	000	015	028	003	0143	363	448		000	000	087	0920	000	000
106	1952	048	000	464	038	000	0457	039	002		000	000	000	0480	474	013
107	1986	014	000	996	008	000	0000	000	000		013	000	000	0009	959	020
108	1984	016	000	001	018	000	0981	000	000		000	017	000	0966	030	000
109	1919	041	040	000	159	006	0648	187	000		000	030	000	0845	140	023
110	1960	040	000	012	028	011	0682	267	000		000	122	014	0846	014	001
111	1970	012	018	000	024	000	0732	041	203		000	000	120	0870	007	000
112	1984	016	000	036	026	000	0938	000	000		003	009	000	0965	000	000
113	1773	131	096	000	012	111	0877	000	000		063	382	000	0547	013	000
114	1885	073	042	000	063	009	0720	173	004		000	000	000	0988	073	000
115	1987	013	000	008	757	000	0102	112	015		000	000	000	0209	821	017
116	1898	102	000	056	247	019	0337	337	004		000	000	008	0755	210	032
117	1987	013	000	059	761	038	0081	061	000		000	015	007	0106	841	016
118	1904	096	000	039	065	028	0868	000	000		123	238	007	0579	035	004
119	1842	158	002	027	120	038	0812	003	000		000	113	002	0825	055	002
120	1950	050	000	048	040	010	0902	000	000		009	103	003	0831	030	023
121	1862	138	000	062	066	020	0787	065	000		000	157	010	0803	023	000
122	1930	070	000	055	026	000	0825	094	000		000	009	020	0963	000	000
123	1926	074	000	016	077	012	0563	313	017		000	000	010	0964	009	004
124	1895	105	000	072	102	010	0826	000	000		154	107	004	0641	067	003
125	1784	151	065	000	180	042	0778	000	000		013	059	005	0901	005	000
126	1815	185	000	120	022	015	0843	000	000		007	053	000	0945	008	000
127	1764	236	000	093	085	013	0809	000	000		017	013	001	0996	000	000
128	1862	138	000	135	062	020	0667	119	000		000	023	000	0863	105	008
129	1842	158	000	037	070	059	0826	008	000		000	139	002	0825	042	003
130	1959	041	000	002	915	017	0011	095	000		000	019	019	0052	913	000
131	1737	263	000	162	049	000	0785	004	000		000	024	000	0997	000	000
132	1818	192	000	087	070	036	0743	064	000		000	072	003	0860	051	004
133	1965	035	000	098	000	000	0902	000	000		094	039	000	0826	026	001
134	1927	073	000	039	068	023	0648	222	000		000	360	018	0573	019	009
135	1934	066	000	039	063	020	0878	000	000		052	594	018	0281	015	018
136	1886	114	000	033	057	027	0805	079	000		000	150	003	0807	044	008
137	1862	138	000	025	041	059	0776	099	000		000	053	007	0895	053	000
138	1732	268	000	024	186	052	0722	016	000		000	119	005	0830	046	001
139	1905	080	015	000	121	012	0549	318	000		000	022	000	0932	032	009
140	1905	075	022	000	037	032	0753	178	000		000	130	003	0836	049	011
141	1947	053	000	009	034	004	0858	095	000		000	039	004	0942	032	000
142	1915	085	000	021	053	008	0733	185	000		000	097	011	0874	031	000
143	1925	075	000	036	058	008	0704	194	000		000	100	014	0852	034	000
144	1898	102	000	004	097	008	0745	146	000		000	109	011	0855	036	000
145	1926	074	000	033	057	009	0760	141	000		000	086	008	0870	038	000
146	1917	083	000	072	042	010	0685	191	000		000	108	006	0828	051	012
147	1914	086	000	029	048	008	0822	093	000		000	091	006	0884	032	000
148	1940	060	000	014	128	008	0577	273	000		000	005	044	0847	104	007
149	1956	044	000	007	095	009	0701	192	000		000	022	014	0859	086	011
150	1872	128	000	006	044	011	0870	069	000		000	114	006	0899	013	000
151	1982	018	000	112	736	018	0033	101	000		000	018	006	0136	870	007
152	1872	128	000	070	072	018	0697	143	000		000	109	009	0836	049	001
153	1910	090	000	019	048	015	0572	346	000		000	009	016	0871	032	000
154	1931	045	024	000	004	007	0949	040	000		000	011	001	1008	006	003
155	1902	098	000	049	041	013	0897	000	000		031	113	004	0830	026	001

* DEPENDENT VARIABLES

TABLE 3. CLINOPYROXENE DATA. OPTICS, SPECIFIC GRAVITY, AND RESIDUALS

NOTE. RESIDUAL E1 = $Y1(OBS.) - Y1(CALC. BY REGRESSION)$, ETC.

NO.	Y1 N(X)	E1 E(X)	Y2 N(Y)	E2 E(Y)	Y3 N(Z)	E3 E(Z)	Y4 Z/C	E4 E(Z/C)	Y5 G	E5 E(G)
001	1.6950	+0.036	1.6980	+0.032	1.7190	+0.041	41.	-02.1	*	*
002	1.6720	-0.151	1.6780	-0.111	1.7010	-0.074	39.	+03.9	3.350	-0.0090
003	1.6840	-0.083	1.6920	-0.062	1.7120	-0.081	39.	-02.9	3.350	-0.0227
004	1.6900	-0.063	1.6970	-0.035	1.7160	-0.058	38.	-03.3	3.370	-0.0067
005	1.6900	+0.018	1.6960	+0.011	1.7180	+0.022	40.	-01.1	3.340	-0.0026
006	1.6950	-0.018	1.7020	-0.011	1.7220	-0.020	41.	+02.4	3.380	-0.0049
007	1.7000	+0.001	1.7060	-0.009	1.7300	+0.020	36.	-02.2	3.380	-0.0200
008	1.6980	+0.003	1.7050	+0.018	1.7240	-0.003	40.	-02.2	3.380	-0.0118
009	1.7040	-0.065	1.7120	-0.039	1.7330	-0.053	39.	-04.4	*	*
010	1.7070	-0.024	1.7150	+0.020	1.7350	-0.002	40.	-00.4	3.420	-0.0055
011	1.7040	-0.038	1.7110	-0.021	1.7330	-0.032	41.	-00.2	*	*
012	1.6960	-0.027	1.6980	-0.082	1.7120	-0.110	45.	-01.8	*	*
013	1.7090	+0.024	1.7130	+0.011	1.7390	+0.042	44.	+01.6	3.490	+0.0517
014	1.7120	+0.036	1.7170	+0.032	1.7380	+0.015	43.	+00.3	3.500	+0.0361
015	1.7180	+0.029	1.7250	+0.043	1.7410	-0.022	43.	+02.4	3.510	+0.0163
016	1.7190	-0.055	1.7260	-0.052	1.7470	-0.060	47.	+01.3	*	*
017	1.7350	+0.075	1.7410	+0.082	1.7610	+0.066	40.	-02.5	*	*
018	1.7370	+0.043	1.7410	+0.020	1.7650	+0.037	43.	-01.4	*	*
019	1.6840	-0.036	1.6910	-0.033	1.7120	-0.030	41.	-02.2	3.370	-0.0044
020	1.7260	-0.007	1.7320	+0.012	1.7630	+0.128	44.	-00.2	3.480	-0.0320
021	1.7470	+0.0120	1.7540	+0.135	1.7720	+0.101	39.	-07.5	*	*
022	1.7450	+0.081	1.7530	+0.103	1.7710	+0.067	41.	-03.9	*	*
023	1.7430	-0.120	1.7510	-0.100	1.7720	-0.102	47.	-00.0	3.650	+0.0157
024	1.6980	+0.103	1.6950	+0.070	1.7220	+0.124	42.	+07.4	3.510	+0.0953
025	1.6900	+0.069	1.6960	+0.083	1.7150	+0.063	*	*	3.360	+0.0297
026	1.6810	-0.064	1.6880	-0.058	1.7100	-0.054	42.	+02.6	*	*
027	1.6900	+0.042	1.6960	+0.044	1.7160	+0.022	*	*	3.360	+0.0133
028	1.6910	+0.007	1.6970	+0.038	1.7180	+0.012	40.	+00.5	3.430	+0.0344
029	1.7090	+0.055	1.7110	+0.040	1.7380	+0.074	*	*	*	*
030	1.7110	+0.081	1.7130	+0.073	1.7390	+0.095	*	*	3.520	+0.0290
031	1.7190	+0.109	1.7220	+0.111	1.7450	+0.094	42.	+00.8	*	*
032	1.6810	-0.006	1.6880	+0.010	1.7090	+0.024	41.	+00.6	*	*
033	1.7130	-0.001	1.7130	-0.019	1.7340	-0.051	*	*	3.580	+0.0341
034	1.7137	-0.051	1.7137	-0.070	1.7417	-0.049	39.	-05.6	3.440	-0.0885
035	1.6715	-0.016	1.6782	-0.010	1.7007	+0.001	39.	-04.0	3.320	+0.0316
036	1.6742	-0.004	1.6800	-0.003	1.7019	+0.001	40.	-01.6	*	*
037	1.6797	+0.017	1.6844	+0.020	1.7058	+0.034	41.	+01.3	*	*
038	1.6810	+0.004	1.6853	-0.001	1.7057	+0.002	40.	+00.6	*	*
039	1.6805	+0.014	1.6852	+0.012	1.7075	+0.030	40.	-00.7	3.299	-0.0123
040	1.6818	+0.009	1.6865	+0.006	1.7085	+0.006	41.	-00.9	*	*
041	1.6825	-0.036	1.6860	-0.057	1.7090	-0.039	41.	-00.8	*	*
042	1.6823	+0.018	1.6874	+0.020	1.7093	+0.020	41.	-00.5	*	*
043	1.6820	-0.008	1.6875	-0.005	1.7101	-0.001	42.	+00.1	*	*
044	1.6832	+0.002	1.6870	-0.005	1.7100	+0.003	42.	+00.7	*	*
045	1.6870	-0.007	1.6921	-0.003	1.7149	+0.000	42.	-00.2	*	*
046	1.6905	-0.004	1.6951	-0.004	1.7190	+0.007	44.	+02.4	*	*
047	1.6924	+0.001	1.6973	-0.008	1.7193	-0.004	42.	-00.5	*	*
048	1.6985	+0.003	1.7055	+0.012	1.7270	+0.015	43.	-01.4	3.414	+0.0105
049	1.6995	+0.007	1.7063	+0.008	1.7280	+0.012	42.	-03.6	*	*
050	1.7080	+0.044	1.7140	+0.048	1.7360	+0.046	43.	+00.6	*	*
051	1.7080	+0.010	1.7145	+0.019	1.7350	+0.010	48.	+03.5	3.397	-0.0598
052	1.7225	+0.003	1.7300	+0.005	1.7505	-0.007	48.	+02.5	3.535	-0.0035
053	1.7355	+0.009	1.7450	+0.021	1.7650	+0.006	56.	+05.7	*	*
054	1.6977	+0.040	1.7055	+0.030	1.7240	+0.003	50.	+01.8	*	*
055	1.6892	-0.018	1.6950	-0.011	1.7164	-0.006	43.	+00.7	3.315	-0.0371
056	1.6925	-0.017	1.6980	-0.016	1.7195	-0.003	46.	+01.9	3.285	-0.0922
057	1.6990	-0.030	1.7048	-0.030	1.7260	-0.025	45.	+02.4	3.445	+0.0475
058	1.7087	+0.027	1.7140	+0.022	1.7339	+0.028	44.	+01.3	3.389	-0.0083
059	1.7154	+0.038	1.7208	+0.032	1.7402	+0.041	46.	+02.6	3.449	-0.0244
060	1.7095	-0.019	1.7153	-0.025	1.7350	-0.031	44.	+00.5	3.449	-0.0458
061	1.7258	-0.003	1.7327	-0.003	1.7550	+0.001	48.	+01.5	*	*
062	1.6930	+0.038	1.6968	+0.033	1.7215	+0.059	44.	+01.9	*	*
063	1.6941	+0.015	1.6984	+0.006	1.7218	+0.015	44.	+02.5	*	*
064	1.6937	+0.008	1.6982	-0.000	1.7221	+0.013	44.	+02.7	3.383	+0.0261
065	1.6954	+0.011	1.7005	+0.011	1.7250	+0.029	44.	+02.8	*	*
066	1.6950	+0.026	1.6990	+0.028	1.7220	-0.033	44.	+03.2	*	*
067	1.6972	+0.007	1.7005	-0.003	1.7240	-0.001	44.	+03.3	*	*
068	1.6950	-0.040	1.7010	-0.019	1.7240	-0.024	44.	+02.4	*	*
069	1.6718	-0.000	1.6785	+0.003	1.7013	+0.009	40.	-00.5	3.281	-0.0109
070	1.6740	+0.016	1.6805	+0.022	1.7029	+0.028	40.	-00.0	*	*
071	1.6915	-0.014	1.6980	-0.023	1.7185	-0.027	45.	+01.3	3.373	+0.0022
072	1.7073	+0.068	1.7140	+0.069	1.7328	+0.056	48.	+02.7	*	*
073	1.7210	+0.065	1.7290	+0.068	1.7463	+0.049	51.	+03.7	3.440	-0.0066
074	1.7000	+0.004	1.7110	+0.011	1.7280	-0.026	51.	+02.0	*	*
075	1.6988	-0.018	1.6980	-0.027	1.7228	-0.038	40.	-00.3	*	*
076	1.7066	-0.003	1.7055	-0.014	1.7325	-0.011	42.	+00.5	*	*
077	1.7095	+0.019	1.7085	+0.005	1.7360	+0.013	40.	-01.4	*	*

NO.	Y1 N(X)	E1 E(X)	Y2 N(Y)	E2 E(Y)	Y3 N(Z)	E3 E(Z)	Y4 Z/C	E4 E(Z/C)	Y5 G	E5 E(G)
078	1.6520	+0.0017	1.6510	+0.0025	1.6610	+0.0005	22.	-00.4	3.190	-0.0192
079	1.6700	-0.0039	1.6760	-0.0043	1.7060	+0.0038	38.	-02.1	*	*
080	1.7550	+0.0046	1.7810	+0.0061	1.7950	+0.0070	92.	+08.6	*	*
081	1.6865	-0.0079	1.6920	-0.0100	1.7130	-0.0103	44.	+01.0	*	*
082	1.6920	+0.0032	1.7000	+0.0051	1.7190	+0.0031	45.	+03.0	*	*
083	1.6860	+0.0046	1.6910	+0.0043	1.7140	+0.0069	*	*	*	*
084	1.7040	-0.0066	1.7110	-0.0049	1.7330	-0.0057	39.	-03.2	*	*
085	1.7260	+0.0016	1.7540	+0.0090	1.7630	+0.0035	60.	-08.7	*	*
086	1.7675	+0.0023	1.8062	+0.0064	1.8230	+0.0078	96.	-03.9	3.587	+0.0156
087	1.7700	+0.0044	1.8110	+0.0094	1.8250	+0.0071	93.	-02.9	*	*
088	1.7690	+0.0038	1.8050	+0.0042	1.8240	+0.0073	94.	-00.7	3.509	-0.0146
089	1.7600	-0.0004	1.7900	-0.0039	1.8100	-0.0002	90.	-05.0	3.591	+0.0327
090	1.7630	+0.0111	1.7800	-0.0012	1.8120	+0.0155	90.	+05.5	*	*
091	1.6860	-0.0029	1.6930	-0.0030	1.7130	-0.0044	40.	-03.4	3.370	+0.0099
092	1.6950	+0.0005	1.7010	+0.0007	1.7190	-0.0036	41.	-02.0	3.405	+0.0431
093	1.7300	+0.0017	1.7480	+0.0028	1.7680	+0.0054	76.	+12.8	3.516	+0.0154
094	1.7420	-0.0031	1.7680	-0.0060	1.7870	-0.0051	88.	+06.2	3.520	+0.0638
095	1.7200	-0.0081	1.7400	-0.0068	1.7570	-0.0076	75.	+08.2	*	*
096	1.7410	+0.0083	1.7410	+0.0024	1.7620	+0.0068	32.	-07.8	*	*
097	1.6640	-0.0017	1.6710	-0.0010	1.6940	-0.0005	38.	-01.8	*	*
098	1.6550	-0.0035	1.6570	-0.0040	1.6750	-0.0036	34.	+02.2	*	*
099	1.6930	-0.0026	1.6930	-0.0035	1.6710	-0.0011	30.	+01.5	*	*
100	1.6520	-0.0009	1.6510	-0.0015	1.6650	-0.0013	20.	-05.4	*	*
101	1.6930	+0.0027	1.6510	+0.0025	1.6600	-0.0004	22.	-00.4	*	*
102	1.6660	+0.0002	1.6725	+0.0004	1.6955	+0.0009	38.	-01.8	3.305	+0.0442
103	1.6900	-0.0224	1.6930	-0.0259	1.7150	-0.0246	38.	-06.3	3.502	+0.0112
104	1.7030	-0.0034	1.7110	-0.0041	1.7320	-0.0030	46.	-00.6	*	*
105	1.7080	+0.0016	1.7180	+0.0024	1.7360	+0.0004	47.	+00.5	*	*
106	1.6660	-0.0045	1.6740	-0.0046	1.6880	-0.0057	45.	-00.9	3.270	-0.0501
107	1.6950	-0.0033	1.6590	-0.0072	1.6670	-0.0073	*	*	3.336	+0.0302
108	1.6674	-0.0020	1.6745	-0.0019	1.6961	-0.0027	*	*	3.256	-0.0210
109	1.7000	-0.0016	1.7080	-0.0042	1.7270	-0.0048	40.	-09.8	*	*
110	1.6960	-0.0028	1.7010	+0.0021	1.7240	+0.0026	*	*	*	*
111	1.6900	-0.0078	1.6990	+0.0082	1.7210	+0.0112	43.	+00.3	*	*
112	1.6660	-0.0017	1.6750	+0.0016	1.6950	-0.0000	39.	-02.1	*	*
113	1.6950	-0.0113	1.7010	-0.0082	1.7280	-0.0032	39.	+02.5	3.300	-0.0736
114	1.6930	+0.0033	1.7010	+0.0030	1.7220	+0.0030	45.	+03.0	3.350	-0.0260
115	1.7630	+0.0065	1.7990	+0.0097	1.8126	+0.0061	86.	+03.8	*	*
116	1.7200	-0.0001	1.7320	-0.0005	1.7520	+0.0016	62.	+05.5	3.501	+0.0093
117	1.7570	-0.0002	1.7860	-0.0034	1.7970	-0.0090	90.	-00.6	*	*
118	1.6900	+0.0026	1.6950	+0.0033	1.7180	+0.0056	*	*	*	*
119	1.6990	+0.0059	1.7040	+0.0035	1.7250	+0.0037	45.	+00.0	3.316	-0.0074
120	1.6760	-0.0025	1.6830	-0.0011	1.7060	+0.0014	39.	-03.8	3.460	+0.1225
121	1.6920	+0.0026	1.7000	+0.0056	1.7140	-0.0013	43.	+01.0	*	*
122	1.6700	-0.0060	1.6780	-0.0033	1.7020	+0.0000	46.	+05.5	3.214	-0.1001
123	1.6930	-0.0036	1.6990	-0.0045	1.7160	-0.0089	*	*	*	*
124	1.6814	-0.0005	1.6861	-0.0010	1.7047	-0.0013	39.	-05.0	3.330	+0.0108
125	1.6950	-0.0030	1.7000	-0.0050	1.7130	-0.0111	43.	-02.9	*	*
126	1.6800	+0.0038	1.6890	+0.0092	1.7060	+0.0067	43.	+05.0	3.300	+0.0107
127	1.6860	+0.0037	1.6940	+0.0069	1.7120	+0.0064	43.	+02.8	3.319	+0.0140
128	1.6870	+0.0004	1.6940	+0.0011	1.7130	+0.0011	41.	-01.7	*	*
129	1.6950	+0.0026	1.7060	+0.0073	1.7200	+0.0001	46.	+03.5	3.200	-0.1045
130	1.7540	-0.0167	1.7910	-0.0162	1.8050	-0.0189	*	*	*	*
131	1.6760	-0.0016	1.6830	+0.0023	1.7020	+0.0035	36.	-01.8	3.312	+0.0023
132	1.6890	-0.0013	1.6940	-0.0021	1.7100	-0.0058	42.	+00.3	3.407	+0.0808
133	1.6816	+0.0165	1.6843	+0.0156	1.7036	+0.0148	42.	+03.9	3.200	-0.0634
134	1.7180	+0.0109	1.7190	+0.0079	1.7420	+0.0083	45.	+00.4	3.460	+0.0114
135	1.6900	-0.0127	1.6910	-0.0196	1.7110	-0.0166	44.	+00.3	3.420	-0.0407
136	1.6930	+0.0019	1.6990	+0.0018	1.7190	+0.0004	43.	+00.4	3.243	-0.1101
137	1.7040	+0.0125	1.7110	+0.0123	1.7320	+0.0119	48.	+06.8	3.373	+0.0711
138	1.7000	-0.0060	1.7060	-0.0078	1.7240	-0.0094	48.	+01.3	3.358	+0.0066
139	1.6923	-0.0109	1.6994	-0.0116	1.7214	-0.0103	43.	-03.5	3.420	+0.0054
140	1.6910	-0.0048	1.6970	-0.0056	1.7180	-0.0064	43.	+01.0	*	*
141	1.6791	-0.0003	1.6843	-0.0020	1.7071	-0.0012	38.	-03.3	3.303	-0.0157
142	1.6868	-0.0039	1.6908	-0.0062	1.7125	-0.0063	40.	-02.2	3.384	+0.0157
143	1.6818	+0.0007	1.6959	-0.0012	1.7210	+0.0023	40.	-02.8	3.385	+0.0153
144	1.6865	-0.0074	1.6909	-0.0102	1.7119	-0.0107	42.	-02.3	3.382	+0.0074
145	1.6911	+0.0039	1.6951	+0.0015	1.7167	+0.0015	39.	-03.6	3.358	+0.0108
146	1.6858	-0.0048	1.6905	-0.0057	1.7139	-0.0030	41.	-01.5	3.364	-0.0182
147	1.6862	+0.0020	1.6908	+0.0004	1.7141	+0.0021	39.	-02.7	3.332	-0.0038
148	1.6972	-0.0037	1.7029	-0.0079	1.7215	-0.0092	42.	-06.0	3.420	-0.0047
149	1.6937	+0.0012	1.6983	-0.0030	1.7157	-0.0066	39.	-07.2	3.364	-0.0220
150	1.6860	-0.0000	1.6906	-0.0015	1.7137	-0.0002	42.	+01.5	3.324	-0.0195
151	1.7310	-0.0025	1.7860	+0.0010	1.8000	-0.0014	89.	+00.2	*	*
152	1.6940	+0.0017	1.7000	+0.0019	1.7220	+0.0033	*	*	*	*
153	1.6940	-0.0074	1.7020	-0.0058	1.7270	-0.0024	*	*	*	*
154	1.6760	+0.0024	1.6840	+0.0042	1.7030	+0.0015	43.	+04.0	*	*
155	1.6820	+0.0032	1.6870	+0.0030	1.7092	+0.0041	*	*	3.330	+0.0225

* INDICATES LACK OF DATA IN THESE CASES

References for Tables 2 and 3

001	Muir, 1951,	no. 1	064	Hess, 1949	no. 30
002	" "	" 2	065	" "	" 31
003	" "	" 3	065	" "	" 31
004	" "	" 4	066	" "	" 32
005	" "	" 5	067	" "	" 33
006	" "	" 6	068	" "	" 34
007	" "	" 7	069	" "	" 35
008	" "	" 8	070	" "	" 36
009	" "	" 9	071	" "	" 37
010	" "	" 10	072	" "	" 38
011	" "	" 11	073	" "	" 39
012	Troeger, 1951,	" 12A	074	" "	" 40
013	Muir, 1951,	" 13	075	" "	" 41
014	" "	" 14	076	" "	" 42
015	" "	" 15	077	" "	" 43
016	" "	" 16	078	Kuno and Hess, 1953, table 1,	" 1
017	" "	" 17	079	Zwaan, 1954,	" 13
018	" "	" 1	080	" "	" 46
019	Larsen, et al., 1936,	" 19	081	Muir, 1953b,	" I
020	Muir, 1951,	" 21	082	" "	" II
021	" "	" 22	083	Muir and Tilley, 1958,	" T'
022	" "	" 23	084	Muir, 1954,	" 1
023	" "	" 3	085	Wahlstrom, 1940,	
024	Kuno and Nagashima, 1952,	" 1	086	Washington and Merwin,	
025	Kuno, 1955,	" 3		1927,	" 1
026	" "	" 5		5 (Ce,Y) and 8 Zr ignored	
027	" "	" 6	087	Washington and Merwin,	" 3
028	" "	" 8		1927	
029	" "	" 9	088	Washington and Merwin,	" 4
030	" "	" 10		1927	
031	" "	" 32	089	Washington and Merwin,	" 5
032	Zwaan, 1954,	" 15		1927	
033	Kuno, 1955,	" 16	090	Washington and Merwin,	" 7
034	" "	" 1		1927	
035	Hess, 1949,	" 2	091	Larsen and Irving, 1936,	" 2
036	" "	" 3	092	" "	" 3
037	" "	" 4	093	Larsen, 1942,	" 7
038	" "	" 5	094	Goranson, 1927,	
039	" "	" 6	095	Zavaritzky, 1946,	
040	" "	" 7	096	Dixon and Kennedy, 1933,	
041	" "	" 8	097	Bowen, 1914,	" 1
042	" "	" 9	098	" "	" 8
043	" "	" 10	099	" "	" 12
044	" "	" 11	100	" "	" 15
045	" "	" 12	101	" "	" 17
046	" "	" 13	102	Hess, 1949,	Fig. VI
047	" "	" 14	103	Schmitt, 1939,	no. p-5B
048	" "	" 15	104	Allen and Fahey, 1953,	" 4
049	" "	" 16	105	" " " "	" 5
050	" "	" 17	106	Washington, 1922,	(Mexico)
051	" "	" 18	107	" "	(Tibet)
052	" "	" 19	108	Zimanyi, 1893,	
053	" "	" 20	109	Foshag, 1928,	
054	" "	" 21	110	Muir and Tilley, 1958,	no. O'
055	" "	" 22	111	Palache, 1935,	p. 62
056	" "	" 23	112	Merriam and Lauder milk, 1936,	
057	" "	" 24	113	Barth, 1931,	
058	" "	" 25	114	Larsen, 1942,	no. 1
059	" "	" 26	115	Wuelfing, 1894,	
060	" "	" 27	116	Larsen, 1942,	" 6
061	" "	" 28	117	Pecora, 1942,	
062	" "	" 29	118	Muir and Tilley, 1958,	" X'
063	" "		119	Wawryk, 1936,	

120	Williams, 1936,	138	Washington and Merwin,
121	Kuno and Sawatari, 1934,	1921,	(Haleakala)
122	Carobbi and Alfani, 1934,	139	v. Eckerman, 1922,
123	Miyashiro, 1958,	140	Kozu and Seto, 1932,
124	Ernst, 1936,	141	Norton and Clavan, 1959, no. 35-1N
125	Lupanova, 1934,	142	" " " " " 35-5N
126	Tilley, 1938,	143	" " " " " 35-6N
127	" " (Ceylon)	144	" " " " " 35-8N
128	Wolfe, 1938,	145	" " " " " 35-9N
129	Williams, 1936,	146	" " " " " 35-13N
130	Miyashiro and Miyashiro,	147	" " " " " 35-19N
	1956, table 27, no. 6	148	" " " " " 35-24N
131	Troeger, 1957 " 5	149	" " " " " 35-25N
132	Deriu, 1959, " VII	150	" " " " " 35-32N
133	Ries, 1896,	151	Sabine, 1950,
134	Wahl, 1907, (Onege L.)	152	Muir and Tilley, 1958, " S'
135	" " (Aland Is.)	153	Shid6, 1958, Table 13
136	Kozu and Washington, 1918,	154	Miyashiro, et al., 1958,
137	Washington and Merwin,	155	Brown, 1956.
	1921, (Etna)		

in a normal distribution should be only 0.012. That is, in the present list of 155 specimens, no more than two or three should be present with deviations in excess of 2.5 σ_p , if the residuals are distributed normally, and if various other hypotheses concerning the data are at least approximately true. Specimens with such large residuals are as follows: Numbers 002, 103, 130, 133 for n_x ; 103, 130, 133 for n_y ; 103, 130, 135 for n_z ; 093, 109 for Z/c; and 120 for G. We shall consider these individually after a word about evidence for linear variation.

5. HYPOTHESIS OF LINEARITY

Henriques (1958c) calculated regression constants for first- and second-degree terms (i.e., coefficients a, b, and c, in $y_p = a_p + \sum b_{1p}x_1 + \sum c_{1p}x_1^2$), for a subsystem of clinopyroxenes consisting of about 40 specimens in the field diopside-hedenbergite-clinoenstatite-clinoferrosilite. As already noted, many of his coefficients were found to be smaller than their own estimated standard errors, so that zero is necessarily included in their uncertainty-ranges, from a purely descriptive point of view, even if (as Henriques pointed out) there may be valid reason for assuming that second-degree terms are theoretically necessary.

The possibility of non-linear variations may be examined by looking for curvature in the relations (if any) between residuals E_p (table 3) and each of the several chemical variables x_1 and z_j (table 2). Hey (1956) pointed out that if the residuals are plotted graphically against each of the independent variables in turn, any evidence of a sloping-straight-line relation indicates an error in the corresponding regression constant b_{1p} , and any curvature in such a line indicates non-linearity of the relation and consequently the need for a more complex formulation of the fundamental relationship of equation (1). Trials indicated that graphical tests are cumbersome for the large number of observations here used, but it is easy to list the data in the order determined by each of the composition variables x_1 and z_j in turn, and several rough checks are available using such lists.

TABLE 4
Regression coefficients for clinopyroxene

Relations between y_p (n_x , n_y , n_z , Z/c , and G , for $p = 1, 2, \dots, 5$) and twelve components x_i of chemical composition. Regression formula is $y_p = \Sigma (b_{ip})x_i \pm s_{ip}$, where y = calculated value, x = independent variable (including $x_0 = 1$, a "pseudovisible"), and s = standard error of regression. Compositions in terms of standard formula $ABCaO_6 = CaMgSiO_6$ for case of all $x_i = 0$.

i Def. of x	$p = 1$		$p = 2$ (n_y)		$p = 3$ (n_x)		$p = 4$ (Z/c)				$p = 5$ (G)	
	x_1	s_{x1}	b_{11}	s_{11}	b_{11}	s_{11}	b_{11}	s_{11}	b_{14}	s_{14}	x_1	s_{11}
0 Constant	1.	0	1.6720	.0014	1.6946	.0014	1.	0	39.9	0.9	1.	0
1 Al in C	.0863	.0723	+ .0469	.0136	+ .0387	.0145	.0878	.0745	-20.5	8.6	.0981	.0668
2 Fe''' in C	.0053	.0153	+ .0404	.0359	+ .0216*	.0381	.0046	.0138	-28.9	25.6	.0048	.0159
3 Al in B	.0468	.0920	- .0567	.0138	- .0714	.0146	.0422	.0525	+ 02.8*	9.7	.0568*	.1227
4 Fe''' in B	.1130	.1973	+ .0889	.0140	+ .0815	.0148	.1143	.1948	+ 58.4	9.0	.0994	.1732
5 Ti in B	.0185	.0200	+ .1198	.0385	+ .1251	.0409	.0190	.0209	+ 16.0*	24.6	.0199	.0192
6 Fe'' in B	.1692	.1982	+ .0598	.0028	+ .0606	.0030	.1782	.2028	+ 02.7	1.8	.1582	.1819
7 Mn in B	.0081	.0518	+ .0345	.0129	+ .0337	.0137	.0088	.0545	+ 08.6	8.3	.0019	.0119
8 Mg in A	.0369	.1486	- .0236	.0035	- .0341	.0037	.0396	.1559	-17.5	2.2	.0275	.1224
9 Fe'' in A	.1379	.1701	+ .0431	.0093	+ .0424	.0037	.1315	.1612	+ 01.5*	2.2	.1368	.1684
10 Mn in A	.0122	.0168	+ .0365*	.0413	+ .0225*	.0456	.0119	.0165	+ 01.6*	29.3	.0111	.0132
11 Na in A	.1074	.2299	+ .0243	.0130	+ .0511	.0144	.1031	.2192	+ 05.8*	8.6	.0990	.2165
12 K in A	.0049	.0069	+ .1093	.0023	+ .0587*	.0909	.0050	.0070	+ 52.2*	55.6	.0050	.0066
No. of obs., N	155		155		155		140		79			
Mean of dependent variable, $\bar{y}$	1.69917		1.70681		1.72787		45.97°		3.3890			
Std. deviation of same, s_y	.02488		.03061		.03027		14.08		.0949			
Std. error of regression, s_p	.0057		.0059		.0063		3.66		.0474			
Mult. coeff. of determination, R^2	.951		.965		.960		.938		.788			
F-ratio	232.		330.		285.		161.		20.			
No. of degrees of freedom for use with F-ratio	12 and 142		12 and 142		12 and 142		12 and 127		12 and 66			

Notes: $y_1 = n_x$ and $y_2 = n_y$ if vibration direction $Y = b$, as in common augite; otherwise $y_1 = n_y$ and $y_2 = n_x$ as in clinopyroxene.
* Entry for which $b_{1p} < s_{1p}$

If the list of residuals E_p , arranged in order of one of the variables x or z , is divided into four equal parts, the summation of E_p should be approximately the same (≈ 0) in each part, unless there are a few observations that do not "belong" statistically to the list. Such individual observations would have residuals far larger than s_p , for example. Similarly, the summation of E_p over the first and last quarters should differ from that over the middle two quarters only if there is a non-linear relation,—again excluding individual observations that contain large errors. Which, if any, of the observations should be excluded from such test procedure is somewhat arbitrarily decided. Also, a simpler but sufficient method is available.

If the list of residuals E_p , arranged in order of one of the variables x or z , is divided as before into four equal parts, the numbers of *positive* residuals in the parts may be used to determine whether the first half of the list is like the last (indicating that the regression constant is without significant error), and whether the combined first and last quarters make a group that is like the combined two middle quarters (indicating non-linear relationship if they differ). This test was applied to each residual E_p in each of the fifteen lists obtained by rearranging the data in orders determined by variables x_1 and z_1 . For variables x that include many zeros only the non-zero observations were considered. Although there is generally no exact equality of the numbers of positive residuals in the two parts of each list compared, the differences are invariably small; significant curvature is not suggested by the data, with the doubtful exception of x_4 (Fe⁺⁺⁺ in position B), which may indicate a curvature of $E_5(G)$ that would require a small positive coefficient of a second-degree term in x_4 for specific gravity, and possibly very small coefficients of second-degree terms in $x_{10}(\text{Mn})$, $x_{11}(\text{Na})$, and $x_{12}(\text{K})$ for Z/c . No curvature is suggested by this test for any refractive index in any other instance.

6. DISCUSSION OF VARIANT SPECIMENS

Nine specimens listed in table 3 have one or more residuals E_p greater than 2.5 times the corresponding standard errors s_p of the regressions. For a single observation, the probability of so great or greater deviation of a normally distributed variable would be 0.012. We have $N = 155$ specimens, each with five residuals for examination (but it is unlikely that the five residuals are independent of one another), so that between two and ten such variant specimens may be considered a fairly reasonable score, assuming that the residuals are normally distributed about zero as mean with s_p as standard deviation. In fact, the standard errors for the most variant specimens would be larger than s_p , so that the criterion adopted overemphasizes residuals for specimens that differ much from the mean composition. The labor of computing the expected standard error for the given specimens is judged too great for the value of the result obtainable. We now identify and discuss these specimens individually.

Specimen 002, augite from the Skaergaard intrusion, Greenland, has an improbably large residual E_1 for n_x , as shown in table 3. The ratio of this residual to the standard error of the regression for n_x is 2.64, which in a normally distributed variable would be exceeded only once in 120 trials. The residual for n_y is more probable (once in 16 trials); those for n_z (.24) and

Z/c (.28) are well within the range of ordinary probabilities. A redetermination of n_x would be interesting.

Specimen 093, aegirine-augite from Iron Hill, Colorado, has an improbable ($<.001$) difference between the observed and the estimated values of Z/c , if the assumptions about normal distribution, linear variations, etc., are correct. Its other properties agree excellently with those predicted by the regressions, and the possibility of an error in the determination of optical orientation may be considered.

Specimen 103, a manganoan ferrosalite from Pewabic mine, Hanover district, New Mexico, has very large negative residuals for all refractive indices. These individually suggest disagreement with one or more of the hypotheses implicit in the regressions (1. linear variations; 2. normally distributed errors in measured physical properties; 3. smaller, and negligible, errors in composition parameters; 4. cations ordered as described; etc.). The combination of such large residuals in all properties indicates much stronger probability that such is the case. The hypothesis of linear variation has already been discussed. That of disorder, or of a different order, among the cations seems unlikely in the present case: the most effective change to a different type of order would seem to be the transfer of all Mn to position B, with equal transfer of Fe'' to A. The hypothesis of disordered distribution of Fe'' and Mn would be less drastic, and would probably produce less change in the properties of the material. The data available (table 4) indicate only small improvements in the residuals due to such exchange of Mn and Fe'' . For example, transfer of all Mn (.045) in A from A to B, and of .045 Fe'' from B to A will affect n_x as follows: For Mn, $b_{r1} = .0292$ and $b_{10,1} = +.0365$, so the transfer of .045 Mn changes y_1 by .045 $(.0292 - .0365) = -.00033$; for Fe'' , $b_{a1} = +.0431$ and $b_{a1} = +.0602$, so the transfer of .045 Fe'' changes y_1 by .045 $(.0431 - .0602) = -.00077$. The total change in y_1 is therefore $-.0011$, a decrease in the calculated n_x and hence an algebraic increase in the residual $E = y(\text{obs.}) - y(\text{calc.})$,—which is in the right direction, but far too small a change to take care of the observed residual of $-.0224$.

The original description of the specimen indicates that the pyroxene was fine grained and contained microscopic inclusions, and one is inclined to wonder whether these inclusions could be manganese- or iron-rich, and therefore responsible for an excess of one of those elements in the analysis. Replacement, for example, of half or more of the Fe'' in position B by Mg would bring the refractive indices estimated by regression approximately into agreement with the observed indices.

Specimen 109, augite from Cerro Mercado, Durango, Mexico, has an estimated extinction angle slightly more than 2.5 times the standard error of regression too large. The refractive indices have residuals well within their corresponding limits, and the reason for the large deviation of Z/c is unknown.

Specimen 120, diopside from minette at Black Rock, Kayenta, Arizona, has a much larger observed specific gravity than would be predicted by the regression. Its other physical properties seem to fit the regressions very well indeed, however. Possibly the specific gravity determination should be rechecked, for it is slightly out of line with usual reports of G for diopside. The

only other specimen with a large residual E_s (on G) is 088, an acmite, with residual $E_s = -.1046 = 2.2 s_s$. That has excellent agreement for refractive indices and Z/c , and there is no explanation for its moderately improbable (.028) residual.

Specimen 130, "aegirine" [acmite] from Kogan-zan district, Korea, has refractive indices that are significantly smaller than estimated by the regressions. Only n_x , n_z , and $2V$ were stated in the original article, but n_y can be calculated with adequate precision even if the optic angle is in error by as much as ± 5 degrees. Because this specimen is rather different from the mean composition ($\bar{x}_1$, table 4), its estimated properties will have somewhat greater uncertainty than those of specimens nearer the mean composition, but this increased uncertainty probably is not great enough to cover the residuals shown in table 3 for the specimen. Several other acmites (086, 089, 093, 094) gave satisfactorily small residuals E_s .

Specimen 133, augite from Pitcairn, New York, was described in 1896, and the consistently large residuals suggest that the analysis may be in error. Actually E_s , the residual on n_x , is slightly within the limit of 2.5 times s_s , but the concurrent evidence of the other two index-residuals which exceed their corresponding limits suggests increased doubt about the agreement for n_x . The original optical data were obtained by fairly precise methods, and the chemical analysis must therefore bear the burden of suspicion. The specimen was included in the study because of superior optical data in spite of the rather old analysis, but it perhaps were better to have rejected it.

Specimen 135, a pigeonite from Åland Island, was described in 1907 and may represent another case of inferior analysis; on the other hand, the original material was fine grained, making accurate optical measurements difficult. The refractive indices are predicted with errors of 2.2, 2.3, and 2.54 times the respective standard errors s_p . Extinction angle and specific gravity, however, are estimated very well by the regressions.

Specimen 117, aegirine from Iron Hill, Colorado, has properties that are generally estimated accurately by the regressions, but its extinction angle differs by 13° , or about 3.5 times s_4 . The reason for this discrepancy is unknown. The analytical result is confirmed to some extent by the excellent agreement obtained between the observed and the estimated values for refractive indices and specific gravity.

7. ACCURACY OF ESTIMATES FOR PARTICULAR COMPOSITIONS

An important step in the least squares solution for the regression constants is the inversion of the moments matrix (in the present case a 13×13 square matrix consisting of the sums of squares of each independent variable, and of the sums of products of each by every other). The inverted matrix is called the covariance matrix; let the matrix be denoted by (C_{ik}) , and its individual elements by C_{ik} , where the subscripts i and k take all values from 0 to 12, inclusive, corresponding to the subscripts of the independent variables (including the "pseudo-variable" x_0) in equation (1). The standard error of any estimated y_p' can be found from equation (3):

$$s(y_p') = s_p (\sum x_i^2 C_{ii} + 2 \sum \sum x_i x_k C_{ik})^{1/2} \quad (3)$$

where the summations are to be taken over all values of i and k , 0 to 12 inclusive, with $i < k$. Different matrices $(C_{ik})_p$ are required for each different set of independent variables x_i —in the present instance, the three distinct matrices involved are $(C_{ik})_{1,2,3}$ corresponding to $p = 1, 2$, and 3 , $(C_{ik})_4$ for $p = 4$, and $(C_{ik})_5$ for $p = 5$. These matrices are given in an appendix at the end of this article, with an example of their use. The standard errors of estimated properties listed in table 5 were computed by equation (3) from the appropriate matrices. From them, standard errors for other compositions can be estimated.

Student's t -ratio (Davies, 1958; Fisher, 1958) can be used to determine with any specified degree of confidence the limits, Y' and Y'' , between which lies the *true* value, y_p^* , corresponding to any given set of x_i -values. The definition may be rephrased as a question (Acton, 1959, p. 34): What numbers Y' and Y'' shall be assigned in order to make an assertion that will be correct 90% of the time (in a long series of such assertions), such that for a given set of x_i -values, the *true* y_p (i.e., y_p^*) is contained in the interval between Y' and Y'' ? The standard error $s(y_p')$ is calculated by equation (3) using the covariance matrix $(C_{ik})_p$; this is then multiplied by the tabulated value of t appropriate for the number of degrees of freedom involved (here, 142 for $p = 1, 2$, or 3 , 127 for $p = 4$, or 66 for $p = 5$) and the desired level of confidence (90%, for example). The product is added to and subtracted from y_p' to determine the required Y', Y'' . For 90% confidence limits, and more than 100 degrees of freedom, $t \approx 1.66$; for 95%, $t \approx 1.98$; for 98%, $t \approx 2.36$; and for 99%, $t \approx 2.62$. Thus we can be "90% sure" that the true value of n_x in diopside (for which all $x_i = 0$ except $x_o = 1$) must lie between 1.6680 and 1.6636; similarly, n_x in hedenbergite lies between 1.7219 and 1.7301; likewise n_x in johannsenite should lie between 1.6443 and 1.6855,—with a range that can no doubt be improved (reduced) by consideration of very few additional, well-chosen specimens. It is well to emphasize again that the statements here made are founded upon a number of statistical assumptions, which are generally reasonable, and with which the data of the 155 specimens here considered are internally consistent; there is no suggestion, however, that the equations (1) are more than descriptively significant.

8. PHYSICAL PROPERTIES OF CLINOPYROXENES WITH INTERESTING COMPOSITIONS

Regressions are not suitable for long extrapolations beyond the limits of the data on which they are based, but we have here an opportunity to compare results estimated by equations (1) and table 4, with published data estimated either by regression or by classical graphic methods. The principal classical end members of pyroxene are considered "interesting" for obvious reasons (of which one is that properties may be estimated by interpolation for intermediate compositions). This is not to imply that such end members have any necessary existence as such in crystals having intermediate composition; they are in fact empirically useful, just as axes of reference are useful in describing a vector. The data presented in equations (1) and table 4 do represent reasonably adequate coverage of the whole clinopyroxene field, however,

so that none of the end members is very far removed from one or more observations actually represented in the data.

Estimated physical properties of interesting compositions are shown in table 5, together with data estimated or measured by other workers using various methods. The agreement is good to excellent between the classical data quoted in the lower part of the table and those obtained by regressions based on table 4; in fact there are only five instances out of the twenty-five available comparisons, where the classical (graphic) datum differs by more than twice the standard error of the regression-derived datum, and if reasonable standard errors of the graphically derived data are applied, the agreement is probably good in all instances. This is not to say, however, that the classical, graphically derived data are necessarily the best: they are, in fact, probably less accurate in most instances; their precision is not known, although of course it may be guessed at by any mineralogist. The precision of the regression estimates based on table 4 is indicated under each estimate. Apparently the classical values need minor revisions.

Henriques (1958a, b, c) and Hori (1954) published separate regression studies of nearly the same group of clinopyroxenes containing little Na, Fe^{III}, or Mn. Their regressions yield different estimates of the physical properties for certain interesting compositions shown in table 5. The basis of Hori's and Henriques' regressions is unfortunately only about 40 specimens, though their data are very homogeneous and probably of superior accuracy. The regressions cannot be expected to yield accurate estimates of properties for the more exotic compositions like johannsenite, jadeite, or aegirine (columns 160, 161, 165, table 5). Their estimates are nevertheless generally in line with data derived with much shorter extrapolation, whether by classical two-dimensional diagrams or by regressions (1) based upon the constants of table 4. The new extrapolations given in table 5 with their respective estimated standard errors are believed to be the best estimates now available, based as they are on a generous sampling of clinopyroxenes of widely different compositions.

Tsvetkov (1951) published some data on synthetic clinopyroxenes that can be used to set up a series of regression equations, each based upon the addition to diopside of a single end-member component. His results can be expressed as follows: Let the formula of the clinopyroxene be expressed as $(1-u_r) \cdot (\text{Diopside}) + (u_r) (W_r)$, where W_r and the maximum limit of u_r are as in the following list: $W_1 = \text{CaAlSiAlO}_6$, $u_1 < .4$; $W_2 = \text{CaFe}^{\text{III}}\text{SiFe}^{\text{III}}\text{O}_6$, $u_2 < .5$; $W_3 = \text{CaTi}^{\text{III}}\text{SiAlO}_6$, $u_3 < .4$; $W_4 = \text{CaTi}^{\text{III}}\text{Al}_2\text{O}_6$, $u_4 < .3$; $W_5 = \text{CaCrSiAlO}_6$, $u_5 < .2$. If values u_r are restricted so that the product of any two different u 's is always zero (i.e., $u_r u_t = 0$ for all $r \neq t$), the equations (4) express Tsvetkov's data very well except for the non-linear cases noted.

$$\begin{aligned} n_x &= 1.644 + .050u_1 + .320u_2^* + .132u_3 + .263u_4^* + .100u_5 \\ n_y &= 1.671 + .052u_1 + .368u_2 + .130u_3 + .254u_4^* + .100u_5 \\ n_s &= 1.694 + .050u_1 + .342u_2 + .112u_3 + .212u_4^* + .096u_5 \\ n(\text{glass}) &= 1.602 + .010u_1 + .358u_2^* + ? u_3 + .226u_4 + .074u_5 \\ Z_c &= 38.5 - 10u_1 + 78u_2^* + 17u_3 + 64u_4 + 24u_5 \\ G &= 3.28 - .28u_1 + .58u_2 + .13u_3 + ? u_4 + .17u_5 \end{aligned} \quad (4)$$

* Non-linear

TABLE 5
Predicted properties of clinopyroxenes with interesting compositions

		Diopside (Di)	Hedenbergite (Hs)	Claconstatite (Ca)	Clinopyroxene (hypersthene (50% Ca))	Jadeite (Jd)	Aegirite (Ae)	Salite (Sa = Di ₅₀ Hs ₅₀)	Augite (An + CaAl ₂ SiO ₆)	Pigeonite
		156	157	158	159	160	161	162	163	164
x_1	Si	2	2	2	2	2	2	2	1.9	1.9
x_1	Al	0	0	0	0	0	0	0	.1	.1
x_2	Fe ⁺⁺	0	0	0	0	0	0	0	0	0
x_3	Al	0	0	0	0	1	0	0	.1	.1
x_4	Fe ⁺⁺	0	0	0	0	0	1	0	0	0
(x_4)	Cr	0	0	0	0	0	0	0	0	0
x_5	Ti	0	0	0	0	0	0	0	0	0
x_6	Mg	1	0	1	1	0	0	.5	.45	.9
x_6	Fe ⁺⁺	0	1	0	0	0	0	.5	.45	0
x_7	Mn	0	0	0	0	0	0	0	0	0
x_7	Mg	0	0	1	0	0	0	0	0	0
x_9	Fe ⁺⁺	0	0	0	1	0	0	0	0	.9
x_{10}	Mn	0	0	0	0	0	0	0	0	0
x_8	Ca	1	1	0	0	0	0	1	1	.1
x_{11}	Na	0	0	0	0	1	1	0	0	0
x_{12}	K	0	0	0	0	0	0	0	0	0
Regression results: best estimates available (equation 1, constants of table 4)										
y_1	n_x	1.6558	1.7350	1.6503	1.7069	1.6560	1.7710	1.6959	1.6941	1.7058
	$s(n_x)$	.0013	.0025	.0030	.0030	.0033	.0027	.0014	.0017	.0034
y_2	n_y	1.6720	1.7318	1.6484	1.7079	1.6647	1.8103	1.7020	1.6960	1.7034
	$s(n_y)$	.0014	.0026	.0031	.0031	.0055	.0028	.0016	.0018	.0035
y_3	n_z	1.6946	1.7551	1.6505	1.7370	1.6745	1.8271	1.7249	1.7186	1.7295
	$s(n_z)$	.0014	.0027	.0033	.0033	.0059	.0030	.0016	.0019	.0037
y_4	Z/c	39.9	42.5	22.4	41.4	48.5	104.0	41.2	39.3	39.5
	$s(Z/c)$	0.9	1.7	1.9	1.9	6.6	2.0	1.0	1.0	1.9
y_5	G	3.261	3.838	3.209	3.619	3.272	3.584	3.400	3.392	3.499
	$s(G)$	.016	.041	.044	.046	.052	.038	.024	.019	.041
Regression results: based on equations 11, 12, and 13 of Henriques (1958a)										
	n_x	1.665	1.731	1.648	1.713	1.661	1.774	1.698	1.642	1.712
	n_y	1.671	1.737	1.646	1.712	1.668	1.803	1.704	1.661	1.710
	n_z	1.694	1.759	1.674	1.759	1.669	1.795	1.725	1.672	1.735
Regression results: based on equations 5, 6, and 7 of Hori (1954)										
	n_x	1.665	1.721	1.652	1.708	1.698	1.673	1.693	1.697	1.710
	n_y	1.674	1.738	1.652	1.716	1.752	1.779	1.706	1.712	1.722
	n_z	1.692	1.756	1.670	1.734	1.769	1.794	1.724	1.729	1.738
Classical data derived mainly by graphical methods (Winchell and Winchell, 1951; Hess, 1948; Tsvetkov's synthetics, 1951)										
	n_x	1.664	1.729	1.654	1.715	1.665	1.776	1.698		
	n_y	1.671	1.740	1.651	1.710	1.659	1.816	1.705		
	n_z	1.694	1.766	1.660	1.735	1.667	1.836	1.725		
	Z/c	38.5	48	22	40	34.5	98	42		
	G	3.3	3.5	3.19		3.356				

Notes: (*) Observed on synthetic material; (A) Synthetic, 60 Diopside + 40(CaAl₂SiO₆);
(b) Interpolated or extrapolated, synthetic

TABLE 5 (Continued)

		Johannesite	Jadeite-Augite (X_{Fe}^{Jd})	Aluminian diopside	Pyrrhotite diopside	Ti-Aluminian diopside	Ti-Aluminian diopside	Clinopyroxene ferrosilite (X_{Fe})	Cr-Aluminian diopside	Actinolite diopside (X_{Fe})
		165	166	167	168	169	170	171	172	173
x_1	Si	o	2	1.6	1.7	1.6	1.6	2	1.6	2
x_2	Al	o	0	.4	0	.4	.4	0	.2	0
x_3	Fe ²⁺	o	0	0	.5	0	0	0	0	0
x_4	Al	b	0	.4	0	0	0	0	0	0
x_5	Fe ²⁺	b	0	0	.5	0	0	0	0	.5
(x_6)	Cr	b	0	0	0	0	0	0	.2	0
x_7	Ti	b	0	0	0	.4	.2	0	0	0
x_8	Mg	b	0	.25	.6	.7	.6	0	.8	.25
x_9	Fe ³⁺	b	0	.25	0	0	0	1	0	.25
x_{10}	Mn	b	1	0	0	0	0	0	0	0
x_{11}	Mg	a	0	0	0	0	0	0	0	0
x_{12}	Fe ³⁺	a	0	0	0	0	0	1	0	0
x_{13}	Mn	a	0	0	0	0	0	0	0	0
x_{14}	Ca	a	1	.5	1	1	.8	1	1	.5
x_{15}	Na	a	0	.5	0	0	0	0	0	.5
x_{16}	K	a	0	0	0	0	0	0	0	0
Regression results: best estimates available (equation 1, constants of table 4)										
y_1	n_x	1.6949	1.6769	1.6706	1.7046	1.7317	1.7079	1.7691	1.6912	1.7335
	$s(n_x)$	.0124	.0028	.0039	.0111	.0118	.0061	.0042		.0017
y_2	n_y	1.7065	1.6833	1.6681	1.7108	1.7387	1.7148	1.7677	1.7024	1.7611
	$s(n_y)$	.0128	.0029	.0040	.0116	.0122	.0053	.0043		.0018
y_3	n_z	1.7232	1.6996	1.6815	1.7266	1.7601	1.7360	1.8867	1.7208	1.7760
	$s(n_z)$	.0137	.0031	.0043	.0123	.0130	.0058	.0046		.0019
y_4	Z/c	48.5	44.8	32.8	48.7	38.1	34.9	44.1	47.7	44.9
	$s(Z/c)$	8.3	3.3	2.9	8.0	7.8	3.4	2.7		1.2
y_5	G	3.617	3.336	3.286	3.639	3.015	3.188	3.797	3.336	3.336
	$s(G)$	.559	.029	.042	.155	.140	.064	.069		.024
Regression results: based on equations 11, 12, and 13 of Henriques (1958a)										
n_x		1.690	1.690	1.690		1.694	1.694	1.778	1.694	1.736
n_y		1.694	1.686	1.680		1.689	1.693	1.778	1.700	1.764
n_z		1.698	1.698	1.694		1.735	1.724	1.804	1.714	1.761
Regression results: based on equations 5, 6, and 7 of Mori (1964)										
n_x		1.700	1.696	1.693		1.733	1.706	1.764	1.693	1.728
n_y		1.702	1.729	1.712		1.727	1.706	1.780	1.694	1.742
n_z		1.732	1.746	1.723		1.756	1.730	1.796	1.716	1.759
Classical data derived mainly by graphical methods (Winchell and Winchell, 1951; Hess, 1949; Tsvetkov's synthetics, 1951)										
n_x		1.710		1.684 ^a	1.758 ^a	1.716 ^a				1.694 ^a
n_y		1.719	1.685	1.692 ^a	1.796 ^a	1.724 ^a	1.721 ^a			1.691 ^b
n_z		1.738		1.714 ^a	1.796 ^a	1.740 ^a	1.738 ^a			1.715 ^a
Z/c	48		39	35 ^a	64 ^a	45 ^a	51 ^a			43 ^a
G	3.5			3.17 ^a	3.45 ^b	3.332 ^a	3.34 ^b			3.31 ^b

Notes: (a) Observed on synthetic material; (b) Synthetic, 60Diopside + 40(CaTiAlO₆);
(b) Interpolated or extrapolated, synthetic

Tests using equation (1) and table 4 on compositions near the maximum variations studied by Tsvetkov (nos. 167, 168, 169, 170, table 5) disagree notably with Tsvetkov's values. However, the extrapolation is great, as shown by the large estimated standard errors. The still larger standard errors for predicting the result of an additional determination (rather than those quoted in table 5 for estimate of the "true value") generally indicate agreement that is as good as can be expected from the data used for constructing table 4.

Tsvetkov measured data on some badly zoned crystals containing $\text{CaTiFe}_2\text{O}_6$ and on some with exotic compositions containing vanadium, but his results for these are not comparable with anything that can be studied by means of the present regressions.

9. DISCUSSION

The practical-minded mineralogist or petrologist may object that most of the preceding development is not directly applicable to his usual problem of deducing chemical composition from the optical properties of a clinopyroxene. This is certainly true, but probably not so hopeless as might be inferred from repeated warnings that these regressions are intended simply as a descriptive tool, and not as a functional representation in the mathematical sense. Several important practical uses are evident at once. One is to estimate the most probable *true* values of the physical properties for selected compositions of interest at the moment—such as those of classical end members, or of an end member modified by certain substitutions of elements, as has been done in constructing table 5. In addition to the best estimate of these properties, the data yield also specific and precise information on the degree of confidence one may place in such estimates, namely the tolerance for any specified level of confidence. If this tolerance seems excessive (compare data on n_x of johannsenite, section 7 herein) the regression study will have served a useful purpose in calling attention to the fact, and probably helping to select critical specimens for further study. An excessively large tolerance for a chosen confidence level may indicate (a) insufficient data, or (b) widely varying, imprecise data among the observations used in constructing the regressions. The residuals (tables 2 and 3) may afford the answer to this question.

Two petrographic applications of pyroxene regressions here presented may be indicated briefly. The properties of a petrographically probable composition may be estimated for comparison with the measured properties of a specimen under study; varying certain components (the x 's in the regressions) may show one or more ways in which the properties of the specimen may be matched. It should be evident that with many more composition-variables than physical measurements no unique solution of the composition is possible, but considerable knowledge from other sources is normally available to the petrologist, and such knowledge can frequently be used to guide him in selection of one of the mathematically possible solutions.

The differences between specific regression constants in table 4 may be used to estimate the effect of a certain *change* of composition. Hori (1954) and Henriques (1958a, b, c) tabulated certain such changes and their effects. More generally, we may simply note the possibility of such tabulations here, and not attempt to list them in detail. For example, table 4 indicates that the

substitution of AlAl for MgSi in any clinopyroxene will change n_x by an amount equal to $b_{11} + b_{31} = .0460 - .0341$, or .0119 increase per unit change in the substitution indicated. Note in this case that x_1 represents explicitly the amount of Si replaced by Al, and x_3 , the amount of Mg replaced by Al. If we varied only x_1 alone, that would still cause a change in z_1 (the amount of Si), but to balance the valency z_3 would also have to change. Similarly if we inquire how much effect the substitution of one Fe'' for Mg would have, the answer is directly given by b_{6p} —it increases n_x , for example, by .0602. Likewise, substitution of Fe'' for Ca affects only x_6 , and the effect on n_x is $b_{61} = .0431$ increase; on the other hand, substitution of NaAl for CaMg decreases n_x by .0098, n_y by .0073, and n_z by .0203, as shown by the sum, $b_{3p} + b_{11,p}$. Other examples will occur to the reader. In every case, the positions C, and B must be maintained exactly full, and A must be under-, or over-filled to balance valency changes unless these are taken care of in the substitution. The relations of the z 's are stated at the foot of table 1.

Evaluation of old or new data may occasionally be possible by checking these data against the self-consistent evidence of nearly all other clinopyroxenes. Occasionally in reading reports of properties of clinopyroxenes, we have discovered descriptions that appear quite inconsistent with the evidence of these regressions. Some instances of this use of regressions are given in the part on selection of analyses, where certain determinations of physical properties seem inconsistent although other physical properties are consistent, or certain chemical analyses can be pointed out as possibly inconsistent because physical properties are consistent with each other, but not with the reported analysis.

As a descriptive device, regressions of optical and other physical properties on the many variables of composition are certainly more effective than charts and diagrams that must be confined to the two dimensions of a sheet of paper, even though several variables may in some cases be shown clearly on a plane diagram. Whenever more than a few—say three or four—variables must be considered, the graphical method is usually awkward at best, and in some cases quite impossible. Of course, the graphical method is more easily used if there are not more than three variables, and in that case the best justification for applying regressions might be that quantitative estimates of precision are desired. Graphical methods tend to bring out non-linear functional relationships rather easily and clearly, and where applicable their advantages must not be overlooked. Multivariate regressions are clearly indicated only when there are many variables to be considered.

A very interesting demonstration now possible for the first time is the essential unity of the entire clinopyroxene system. Perhaps still more components should be allowed for, but additional data may be required to do so effectively. The empirical success of this regression study tends to confirm the gross unity of the clinopyroxenes; it also tends to confirm the hypothesis that the physical properties here considered are indeed linear, additive functions of the chemical composition when that is expressed in terms of an ordered distribution of elements over the several possible crystal-lattice positions.

The gross unity of the clinopyroxene system thus confirmed is not at variance with the known differences in crystal structure (Morimoto, Appleman, and Evans, 1959) that even go so far as to include change of lattice type and space group symmetry in the interval between pigeonite and augite, for those changes are changes in fine structure that affect only a few atoms, permitting small displacements that would tend to make rather small changes in optical properties and specific gravity. Any secondary, smaller differences associated with them should show up in the residuals (table 3) after removal of the variation due to regression. Very careful and detailed study will be necessary to measure any such differences; they are not apparent in the data as presently arranged (or rearranged).

APPENDIX

Computation of standard deviation of estimated value y'_p .

For a given set of values of the independent variables x_i the corresponding values y'_p of the dependent variables can be estimated with the aid of the regression equations at the head of table 4, using the coefficients in that table. Next it is important to be able to estimate the reliability of these values. The standard deviation $s(y'_p)$ of such an estimate is obtained by substituting the same values x_i in the following equation:

$$s(y'_p) = s_p [\sum x_i^2 C_{11p} + \sum \sum x_i x_j C_{1jp}]^{1/2} \quad (3)$$

where $0 \leq i < j \leq 12$, and the C_{ijp} are elements from the p^{th} covariance matrix as given in table 6, all other symbols as hereinbefore defined.

As an example of such a calculation, we consider $s(y'_1)$, the standard deviation for the calculated value of n_x , for the jadeite component $\text{NaAlSi}_2\text{O}_6$. The column headed "jadeite, 160" in table 5 shows that for this composition the independent variables x_i are all zero except x_0 , which is always 1, and x_3 and x_{11} , which are both 1.000 for this composition. Substitution in the above equation gives the following:

$$\begin{aligned} s(y'_1, \text{jadeite}) &= 0.00571 [1^2(.053) + 1^2(5.403) + 1^2(5.214) \\ &\quad - 2(1)(1)(.076) + 2(1)(1)(.014) - 2(1)(1)(4.840)]^{1/2} \\ &= 0.00571 \sqrt{0.866} \\ &= 0.0053 \end{aligned}$$

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REVIEWS

Crystals and the Polarizing Microscope—a Handbook for Chemists and Others, 3rd ed.; by N. H. HARTSHORNE and A. STUART. P. xv, 557, 339 figs., 1 folding plate. London, 1960 (Edward Arnold, Ltd.), New York, 1960 (St. Martin's Press, \$17.50).—As the preface tells us, this book was originally written "with the main objects of making the chemical applications [of polarized-light microscopy] more widely appreciated, and of providing the chemist with a manual in which the method is treated with special reference to his particular problems." This intention is still evident; with increased interest in the subject the book has been expanded and some advanced topics introduced. The table of contents lists chapters on the following subjects: crystalline state, stereographic projection, morphology of crystals, optical properties of crystals, polarizing microscope, preparation and mounting of material, microscopic examination of crystals (i) orthoscopic observations ("parallel light"), (ii) conoscopic observations ("convergent light"), liquid crystals, rotation apparatus and the universal stage, special methods, methods of attack and experiments, examples. A four-page appendix gives general references and works on some particular groups of compounds; a folding plate, "Nomogram for the determination of refractive indices," shows Mertie's solution of the relation between indices and optic axial angle.

The chapter of experiments is well done; however, one feels that it should be extended to facilitate the use of the book as a text.

Material new in this edition includes a brief but very good discussion of the mechanisms of crystal growth, and some additional material on twinning. The chapter on the polarizing microscope contains a discussion of illumination. The treatment of the universal stage in a chapter by itself is new; the chapter of special methods has been extended, mostly by the discussion of hot and cold stages.

The book is intended more for chemists than for mineralogists and geologists. Much of it is excellent material for all students of crystal optics, even though the choice of chemical examples and certain special topics focuses primary attention on the chemists' requirements.

PETER LEAVENS

Terms used in Archaeology, a Short Dictionary; by CHRISTOPHER TRENT. P. 62. New York, 1959 (Philosophical Library, \$2.75).—Archaeological publications tend to be oriented towards the areas in which their authors have worked, and this volume is no exception. It is mostly concerned with the British Isles, covers the continent of Europe and the Near East less adequately, has a few references to the American Indian civilizations, and omits the rest of the world. Included are the names of important sites, peoples, and cultures, as well as terms for types of sites and of artifacts. The definitions emphasize context rather than content.

IRVING ROUSE



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CLIMATIC CHANGES SINCE THE LAST INTERGLACIAL*

RICHARD FOSTER FLINT¹ and FRIEDRICH BRANDTNER²

ABSTRACT. Six curves, from European and American localities, showing inferred fluctuations of climate (chiefly temperature) during various segments of the time since the last interglacial, are compared. The curves are time calibrated by C^{14} dates. Agreement among the curves is very good. Comparison with curves based on isotopic temperatures, derived from pelagic Foraminifera in deep-sea sediment cores, also shows good agreement. It is concluded that a broad pattern of fluctuation of climate, within the time range considered, is becoming evident.

INTRODUCTION

Climatic changes, chiefly in middle latitudes of the northern hemisphere, that have occurred since the last major interglacial have been the subject of both research and speculation. Stratigraphy and C^{14} dates indicated, as early as 1955 (Flint and Rubin, 1955, p. 657-658), the probability of post-Sangamon glaciation older than the generally recognized Wisconsin glaciation. In the same year the important curves published by Emiliani (1958 and earlier papers cited therein), derived from research on deep-sea sediment cores, were a first attempt at showing this sequence of climatic changes on a basis of direct paleotemperature measurement, with at least partial time calibration. Time control, however, was not extensive, consisting of control by C^{14} dates through about the last 27,000 years, with extrapolation farther back in time based on assumed rates of sedimentation.

Subsequently several curves based on continental rather than sea-floor data, chiefly from cores, were constructed and some were published. Although only one of these is based on a complete sequence of temperature inferences reaching continuously back to the last interglacial, from a single locality, five of the curves are time calibrated by C^{14} dates, at least to a first approximation, through a greater time range than the curves from sea-floor data published hitherto. This was made possible by the isotopic-enrichment technique developed by Hessel de Vries and associates at the Groningen C^{14} laboratory. All dates are quoted on a basis of a C^{14} -half-life value of 5568 ± 30 years.

With the object of gaining a clearer picture of the climatic changes since the last interglacial we have compared continental data from Denmark, the Netherlands, Lower Austria, southeastern California, the Great Lakes-St. Lawrence region, and equatorial Colombia, using a uniform scale for time and, as far as the data permit, for temperature also. The data are reproduced in figure 1 and are commented on in the following paragraphs.

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DENMARK AND THE NETHERLANDS

The data from these two areas consist of the curves published by Andersen, de Vries, and Zagwijn (1960). The curves are based on pollen analyses of samples selected from and assembled in stratigraphic sequence according to C^{14} dates. The C^{14} sample numbers and dates are given in the paper cited. The chief localities represented are the Brørup Hotel Bog in Denmark and the vicinity of Amersfoort in the Netherlands. The far ends of both curves, in the

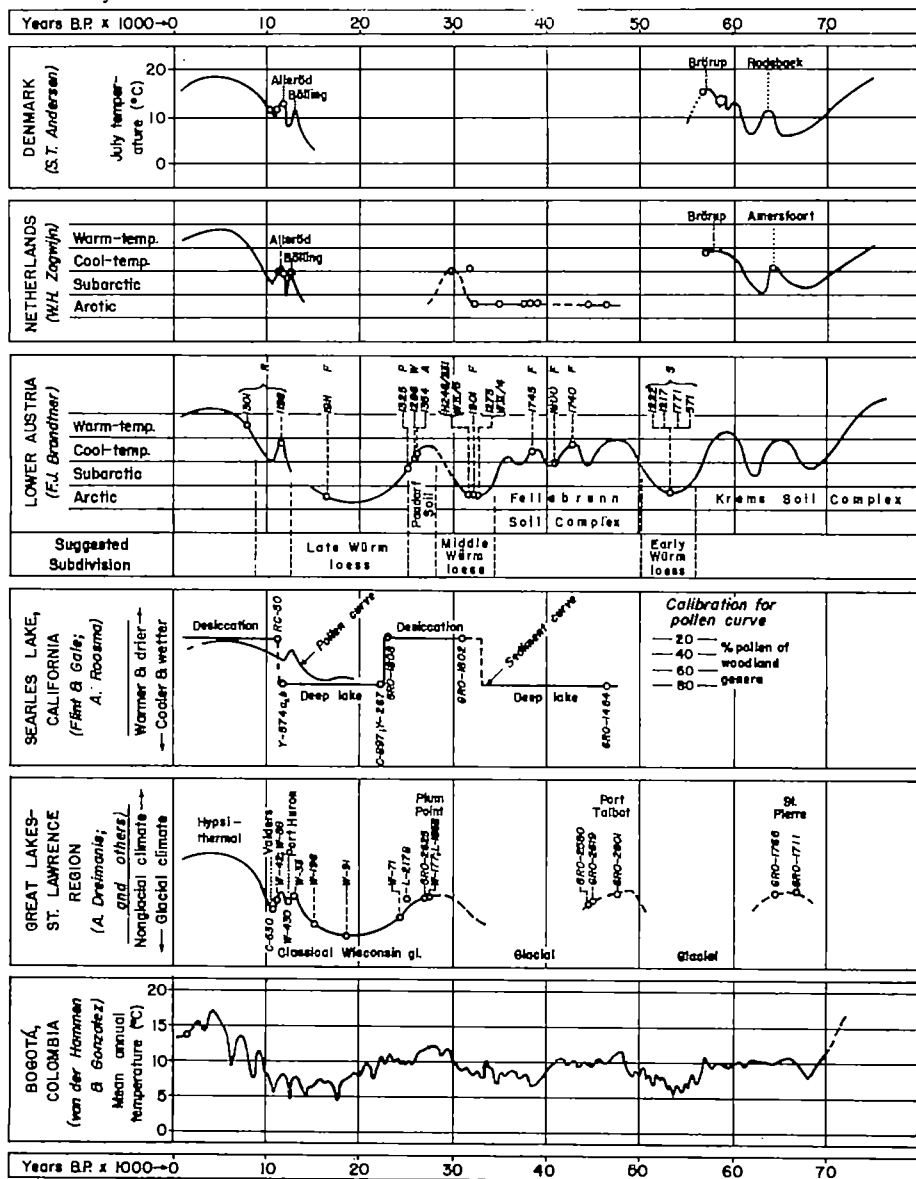


Fig. 1.

vicinity of 70,000 years B.P., are considered by the authors cited to belong to the end of the last (Eem) Interglacial.

LOWER AUSTRIA AND ADJACENT REGIONS

The curve for Lower Austria summarizes the climatic implications of a regional sequence of loess layers and ancient soils and is based chiefly on paleopedologic evidence. The stratigraphic succession is documented by a large number of sections showing the same physical and chemical characteristics (Brandtner, 1950, 1954, 1956; Fink, 1954, 1956). Even the very late part of the sequence, derived from pollen-analyzed lake sediments and peat layers, is preserved, so that correlation is well controlled.

The loess layers occurring between the soils imply cold, dry-continental climates. It is inferred from faunal evidence, mainly mollusks, that the loess overlying the interstadial Paudorf Soil, i.e. the Late Würm loess, marks the coldest phase of the last glaciation cycle. This inference is based on the presence, in increasing numbers, of boreal-alpine and arctic species, which occur sporadically or not at all in pre-Würm and Early-Würm loesses. The temperature decrease, which culminated probably around 20,000 years B.P., was interrupted several times by warmer phases, during which soils formed.

On the curve, in chronologic sequence, are shown the Krems Soil (correlated with the interglacial (marine) Eem deposits), two soils antedating the Early Würm, the Fellabrunn Soil Complex, and the Paudorf Soil. The Krems Soil and its two immediate successors are reddish brown, completely leached soils that indicate moderately warm and humid climates. The properties of the second post-Krems soil, however, suggest an interval longer and considerably warmer than that implied by the first one.

The succeeding Fellabrunn Soil Complex (the Stillfried Complex of Fink, 1954) represents the time unit known as the Göttweig Interstadial. It is preserved completely only within the dry loess province where it has not later been truncated by solifluction or other movement. It consists of a reddish brown leached zone and three calcareous Chernozem soils, all separated from each other by thin, somewhat humic loess. The complex indicates considerably cooler, fluctuating climates that gradually became more continental.

Fig. 1. Climatic variations in middle north latitudes and at an equatorial station, within the last 70,000 years, inferred from terrestrial data. Circles show positions of C¹⁴-dated samples.

Denmark and Netherlands curves (reproduced directly from Andersen, de Vries, and Zagwijn, 1960) are based on pollen data; continuous lines indicate continuous pollen stratigraphy. Temperature calibration differs somewhat between the two curves.

Lower Austria curve, composite for a region, is based on a stratigraphic sequence of loess sheets and soils. The C¹⁴ date prefixed "H" is from the Heidelberg laboratory; all the others are from the Groningen laboratory. Localities: F—Fellabrunn; P—Pollau (= Pavlov); W—Unter Wisternitz (= Dolní Věstonice); W II/5 or 4—Willendorf site II, layer 5 or 4; S—Senftenberg; R—Roggendorf.

Searles Lake curves are based on physical/chemical characteristics of lake sediments and on pollen, as indicated. Pollen curve is from Roosma (1958).

Great Lakes-St. Lawrence curve is composite, having been compiled from a variety of sources (notably de Vries and Dreimanis, 1960) within a rather wide region. The two pre-classical-Wisconsin glacials are based on glacial drift; the nonglacial segments on peat and gyttja.

Colombia curve (from van der Hammen and Gonzalez, 1960, p. 305) is based on pollen data.

The Paudorf Soil, only one foot thick, is closely related to leached Chestnut soils that occur at present beneath certain *Artemisia* steppes in Roumania. It implies a fairly short interstadial, somewhat more humid and perhaps slightly warmer than the intervals during which the uppermost Chernozems of the Fellabrunn Complex were formed.

The chronology of these climatic events is fairly well controlled by C^{14} dates. Although the beginning of the Paudorf Interstadial is still not dated, its end seems to be satisfactorily fixed in time. Charcoal from two archeologic horizons within the top of the Paudorf Soil and immediately above it yielded these dates:

Gro-1286: $25,600 \pm 170$ (Dolní Věstonice, South Moravia) (de Vries, 1958).

Gro-1354: $25,700 \pm 280$ (Aggsbach, Lower Austria; unpublished; monograph in preparation by Brandtner).

A third charcoal sample from an archeologic horizon approximately one foot above the Paudorf soil dates $24,800 \pm 150$ (Gro-1325, Pavlo, South Moravia) (de Vries, 1958).

As to the duration of the much-discussed Göttweig Interstadial, there is still some uncertainty. Charcoal samples from three archeologic layers at the site Willendorf II only postdate the interstadial. However, the oldest and most reliable radiocarbon date obtained from Willendorf II, Layer 4 (Gro-1273: $31,840 \pm 250$) (de Vries, 1958; Brandtner, 1959) is in excellent agreement with the date (Gro-1901: $31,600 \pm 500$) obtained from a loess sample taken immediately above the Fellabrunn Soil Complex in its type section. Further samples taken at the same locality from several horizons of the soil complex itself yielded fairly reliable dates for the lower parts of the Chernozem, as indicated in the curve. The dates are, from top to bottom: Gro-1745: $37,600 \pm 700$; Gro-1800: $42,700 \pm 1,400$; Gro-1740: $41,900 \pm 800$) (de Vries, 1959). The reddish brown zone of decalcification (or loamification) at the base of the soil complex did not contain sufficient humus for measurement.

The beginning of Göttweig-interstadial weathering is merely antedated by a sample taken from a charcoal lens at the Senftenberg locality in Lower Austria. The lens lay within the lower part of the (truncated) zone of weathering a few inches above the C-Ca horizon. The age of the charcoal, however, is not clear. Three different runs gave three different dates: Gro-571: $51,000 \pm 5,000$; Gro-1222 & 1217: $48,300 \pm 2,000$ (de Vries, 1958), and Gro-1771: $> 52,000$ (unpublished).

An additional charcoal sample, secured from the same place in 1959, may yield a reliable date.³ Meanwhile it is certain that the Göttweig Interstadial, during which the Fellabrunn Soil Complex was formed, is much younger than Brørup.

³A monograph on the section at Senftenberg, which contains a paleolithic layer (excavated in 1952 by Brandtner) is in preparation. A brief discussion of the report by Fink (Felgenhauer, Fink, and de Vries, 1959) is in press (*Current Anthropology*). A critical evaluation of the C^{14} dates obtained by de Vries from the Fellabrunn soil complex will be published by Brandtner in *Eiszeitler und Gegenwart*, 1961.

SOUTHEASTERN CALIFORNIA

The curve for southeastern California was constructed from data published by Flint and Gale (1958) and by Roosma (1958). The rectilinear graph reflects the character of lacustrine sediments in the stratigraphic sequence underlying Searles Dry Lake, in the Mojave Desert region, as observed in a series of cores. The graph segments labeled *Deep lake* represent fossil-bearing sediments related to lake water that was deep although saturated, most of the time, with carbonate compounds carried in solution. Such sediments imply a climate cooler and moister than the existing climate. The segments labeled *Desiccation* represent evaporites, implying a climate warmer and drier than that under which the deep lake existed. The amplitude of fluctuation of temperature and/or precipitation is not known from the physical evidence, although fossil invertebrates suggest that mean July temperature may have been at least 4°C.

The vertical slopes connecting the two groups of segments indicate merely sharp changes in the kind of sediment present in the cores. They do not therefore reflect the rate of temperature/precipitation change. If the actual rates were known, undoubtedly the slopes would be curves rather than rectilinear in form. A truer picture of the climatic change in the later part of the time represented is given by the pollen curve, likewise constructed from core sediments. This curve is based on proportions of woodland genera (essentially *Pinus* and *Juniperus*) to desert shrubs and herbs. The lower limit of range of these woodland genera today lies at an altitude about 3400 feet higher than Searles Dry Lake. If the effect of probable changes in precipitation is neglected, and if it is assumed that the difference in altitude is solely the result of change of temperature, the difference corresponds to a temperature change of about 6°C. Using physical evidence only, Meinzer (1922, p. 549) arrived at a crude regional difference of 8°C, probably a limiting maximum value.

The pollen curve shown herewith is taken from the generalized curve in Roosma's figure 1. However, inspection of the more detailed curve in the same figure shows two minor "cold wet" troughs, close together, rather than one only, at the end of the last deep-lake phase. Possibly these are equivalent to the Valders and Port Huron troughs shown on the Great Lakes curve. With C^{14} dates on samples from appropriate positions on the core used in the pollen study, the possibility could be tested.

We have not included the curve developed from the Saltair core (Eardley and Gvosdetsky, 1960, pl. 1) in the basin of ancient Lake Bonneville because it is not controlled by finite C^{14} dates. However, as its authors noted, it shows a considerable extent of agreement with the Searles Lake curve.

GREAT LAKES—ST. LAWRENCE REGION

The curve for this region is drawn from various sources. The segments that represent events antedating 25,000 years B.P. are based on data published by de Vries and Dreimanis (1960), Dreimanis (1960, p. 112), and Terasmae (1957). The segment representing events postdating 25,000 years B.P. is based on a variety of data, originally assembled by Flint and Rubin (1955) and Flint (1956). The C^{14} dates plotted on the curve are selected representative

dates only. References to original publication of these dates are given in the papers cited.

In the younger part of the curve several points are based on geographical positions of the border of the advancing or retreating ice sheet, fixed by over-ridden trees, driftwood imbedded in lake-beach sediments, and similar occurrences. There is therefore no direct basis for determination of temperature, other than that suggested by the ecology implied by tree genera. Hence the curve amplitudes are not calibrated. In the older part of the curve the points are based on wood imbedded in till and on the pollen ecology of *gyttja* and peat in place. The interstadials, labeled St. Pierre, Port Talbot, and Plum Point* in accordance with the literature, were marked by generally boreal climate, in which temperatures did not rise to equal those prevailing today. The peaks of the interstadial curves, therefore, are drawn lower than the peak of the postglacial curve. We emphasize, however, that temperature calibration remains for the future, and that in the present curves we attempt no more than to suggest relative temperature.

COLOMBIA

The curve from Colombia was elaborated by van der Hammen and Gonzalez (1960) from the pollen sequence contained in the uppermost 32 meters of a long core. This was taken from lake sediments in the Sabana de Bogotá (Lat 4°30'N), the floor of an ancient lake now dry, at an altitude of about 8550 feet. By comparing the frequencies of pollen of low-temperature indicators and moisture indicators with the altitude-distribution of the same plants today, these authors derived a curve showing fluctuation of temperature with depth in the core. The plant associations showed further that, in general, annual precipitation tended to decrease with rising temperature. Except in the extreme upper part of the core, stratigraphic position is not time calibrated by C^{14} dates, but amplitude of the curve is calibrated in terms of mean annual temperature. The version of the curve shown in figure 1 was arrived at (with Professor van der Hammen's concurrence) by fitting that part of the curve correlated by van der Hammen and Gonzalez with the Würm Glacial plus the Holocene, to the 70,000-year length of the other curves shown in figure 1. The agreement among major cold and warm intervals is good, as van der Hammen and Gonzalez noted (p. 307) when they compared the Bogotá curve with a generalized curve for the same period in Europe, prepared by Gross (1958).

DISCUSSION OF THE ASSEMBLED CURVES

Agreement among the curves is good. The fluctuations are of the right sign, which is all that can be expected because they are not calibrated in the same way. The curve that is most completely controlled stratigraphically is the Colombia curve, but it is not time calibrated. Probably the Lower Austria curve affords the best overall documentation, when both stratigraphy and chronology are considered. The discrepancy between it and the Netherlands curve, between about 34,000 and about 48,000 B.P., is more apparent than real.

* The names of all time units shown in figure 1 are placed there for reference only. All have been published previously. No proposal or indorsement of any of them as stratigraphic terms is implied.

The Netherlands area was relatively close to the Scandinavian Ice Sheet and may have been too cold to permit reforestation and thus provide pollen documentation of minor fluctuations of climate.

Apart from this discrepancy, and despite the fact that statistical errors in the dates allow for some changes in curve slopes, the similarities lead to the inference that in several middle-latitude regions of the northern hemisphere and in equatorial South America climatic fluctuation has been broadly similar during the last 70,000 years. Likewise the European curves are compatible with the concept, long current among central European geologists, and based on different sorts of evidence in considerable part derived from the Alps, that during this time range there were three principal cold episodes, designated by various names but known most widely as Early, Middle, and Late Würm. The oldest of them is younger than the last major interglacial (Eem Interglacial) in Denmark and the Netherlands (Andersen, de Vries, and Zagwijn, 1960).

Although incomplete, the American curves likewise are compatible with the concept of three cold episodes. If the relation of the Eem to the Netherlands-Denmark curves is accepted, the end of the Sangamon Interglacial in North America is to be looked for within the time segment preceding the St. Pierre Interstadial.

COMPARISON WITH DEEP-SEA SEDIMENT CURVES

Comparison of the curves shown in figure 1 with the isotopic-temperature curves elaborated by Emiliani (1958) from deep-sea cores also shows general correspondence. The agreement supports the contention of Emiliani that temperatures in the glaciated regions of the northern hemisphere were related in time to the surface-seawater temperatures in the tropics. It is true that some details clearly shown in our figure 1 appear only faintly in Emiliani's curves and that others are not represented at all. It is expectable, however, that minor fluctuations of air temperatures at continental stations should be damped down when translated into surface-seawater temperatures at tropical stations. Apart from this, smoothing of the temperature record may have occurred through reworking of sea-floor sediments by bottom-living organisms.

SUMMARY

Six curves, in which climate is plotted against time controlled by C^{14} , and which are derived from localities in Europe and the Americas, are in good agreement. Although very incomplete as a group, they combine to give a general picture of the sequence of climatic changes in various parts of the northern hemisphere since the end of the last interglacial age. They agree also with curves showing fluctuation of surface-water temperature, with time, in tropical seas.

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HIGH TEMPERATURE ACID ROCKS ASSOCIATED WITH SERPENTINITE IN EASTERN QUEBEC

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ABSTRACT. Highly serpentinized alpine-type peridotites frequently have small, relatively acid rock lenses associated with them. Weakly serpentinized or unserpentinized peridotites are usually associated with segregations of olivine gabbro. A study of the acid rocks found in the highly serpentinized peridotite at Asbestos in Eastern Quebec indicates that they are metasomatically altered gabbro bodies. The initial alteration was to a biotite-saussurite which was further altered to a microcline-diopside-albite-quartz rock. The degree of alteration was dependent on structural attitude. These rocks represent high temperature alteration in the amphibolite facies which indicates that the serpentinization of the surrounding peridotite has taken place at a higher temperature than is represented by the general level of regional metamorphism, the epidote-amphibolite facies. Chemical evidence suggests that the components which were added to the gabbros may have been derived in part from the peridotite undergoing serpentinization.

INTRODUCTION

The association of small, relatively acid rock bodies with alpine-type serpentinized peridotites has been noted frequently by geologists working on serpentinites. The term "acid" is used in a relative sense in that actual silica contents may range from 40 wt.% to 80 wt.%. As this implies, the variations in mineralogy are large when the numerous world occurrences are considered and may even be large in a small area. Thus, "acid rocks" is here meant to distinguish those small, usually light-colored, lenslike and dikelike bodies that are found in highly serpentinized alpine-type peridotites and never make up more than 10 vol.% of the serpentinite mass.

The acid rock types usually found in this association include albitites, corundum albitites, alaskites, hornblende, and biotite granites, edenite amphibolites and calc-silicate rocks. Commonly these acid bodies have been considered late-crystallizing silica and water-rich residues of the peridotite magma and, as such, have been used as a source for the silica and water required to serpentinize ultramafic masses (DuToit, 1919; Gordon, 1921). Larsen (1928) has shown that this process is quantitatively impossible. At the present time, they are considered metasomatic and hydrothermal in origin (Turner, 1960; Larsen, 1928; Bowen, 1956, p. 132).

The work undertaken here traces the chemical and mineralogical changes that have affected a particular suite of such rocks in the serpentinite sill at the open pit of the Jeffrey Mine of the Canadian Johns-Manville Company, Ltd. at Asbestos, Quebec (fig. 1).

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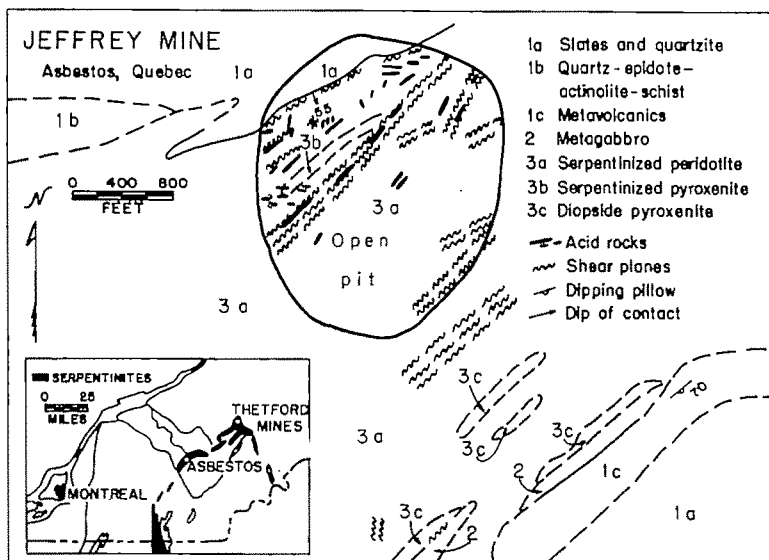


Fig. 1. Geologic sketch map of the open pit and immediate surroundings, Jeffrey Mine, Canadian Johns-Manville Co., Ltd., Asbestos, Quebec.

THE JEFFREY SERPENTINITE AND IMMEDIATE SURROUNDINGS

In this locality the serpentinite sill is 4000 ft thick and was emplaced between underlying siliceous slates, quartzites, and actinolite schists, and overlying metagabbro and metavolcanics (metabasalt and metaandesite) of the Caldwell Series which is of possible Grenville Age (Riordon, 1957). The upper contact is nowhere exposed so that it is impossible to ascertain the genetic relation, if any, between the gabbro and the ultramafic sill. These overlying rocks exhibit retrograde effects characteristic of the epidote-amphibolite facies. Basic plagioclase is altered to clinozoisite and oligoclase, and clinopyroxene is altered to actinolite and chlorite. The underlying metasediments are altered to minerals characteristic of the same facies. The lowermost Caldwell (Bennett Schists, not shown in fig. 1) locally carry hornblende, garnet, kyanite, and staurolite. The rocks immediately underlying the serpentinite consist of quartz, magnetite, and graphite with accessory muscovite, carbonate, oligoclase, and (corroded, detrital) microcline. Within this rock (1a, fig. 1), contact thermal effects are visible, in thin section only, for a distance of at most 4 inches away from the contact. Here minute sillimanite needles are sparsely developed and are associated with clouded Ab80 and fine grains of fresher-appearing Ab65. Some microlites of diopside are associated with corroded grains of primary carbonate. This development of andesine-diopside-sillimanite indicates hornfels development in the amphibolite facies. Beyond a few inches no hornfels minerals are found. A portion of the lower contact consists of actinolite-epidote-albite-quartz-magnetite schist (1b, fig. 1). The actual contact of this rock with serpentinite is not visible so that nothing is known of a hornfels development in it also.

The peridotites of the eastern Quebec "belt" average over 50 vol.% serpentinite (Cooke, 1937, p. 67). At the Jeffrey Mine the mass is virtually 100% serpentinite. The present mineralogy consists of three serpentine minerals (antigorite, chrysotile, and bastite), magnetite, and accessory amounts of presumably primary chromite. In some thin sections small amounts of talc and/or chlorite and/or brucite are found. Nickel (1958) has found traces of iron-nickel alloy (FeNi_3) in samples from Jeffrey. Minor amounts of millerite, pyrite, and diamond have been found in the past.

Because of the high degree of alteration, primary silicates are rare. They consist of Fo 90 (analysis 1, table 1) and En 93 (analyses 2, 3, table 1). The latter always contain exsolution lamellae of diopside (ext. angle = 37°) which results in about 2% CaO in the analyses. The upper third of the sill contains lenses of very coarse-grained diopside pyroxenites (analysis 4, table 1) which have been only superficially serpentinized along fractures and cleavages.

On the basis of abundance of bastite pseudomorphs after orthopyroxene, it was possible to distinguish one band in the lower third of the sill, which is dominantly a serpentinized orthopyroxenite (3b, fig. 1). However, it was found that the absence of such pseudomorphology is not a good criterion for designating a rock as serpentinized dunite. Many hand specimens show no bastite whereas their thin sections carry large amounts of fine-grained bastite crystals and orthopyroxene remnants that are usually brecciated and bent (pl. 1-E). This feature was also noted by Guild (1947), and Cooke (1937). Cooke (p. 70) suggests that the retention of bastite pseudomorphs depends on the original grain size of orthopyroxene. Tectonic activity that accompanies serpentinization results in a cataclastic texture whereby pyroxene and bastite are reduced in size and only the coarsest original grains are still evident in hand specimens. In this regard it must be noted that the upper third of the sill never carries any bastite even in thin sections. Company geologists have speculated that it may represent a serpentinized dunite. However, it is not designated as such in figure 1 because of the lack of corroborative evidence of any kind.

It was noted earlier that the serpentinite contact with the overlying rock types is not exposed, and that the partially exposed lower contact shows a weak hornfels development for a few inches into the metasediments. It must also be noted that this lower contact is quite irregular, and serpentinite in places is found mechanically squeezed into joints and fractures for several inches into the metasediments. Immediately to the west of the pit an arm of serpentinite protrudes into the metasediments for about 700 ft (fig. 1).

Within the Jeffrey serpentinite relatively acid rocks are found occurring as lensoid masses rarely over 60 ft in diameter and 15 ft thick. They are confined to the lower half of the sill and comprise about 5 vol.% of the whole mass in this locality. For purposes of description, biotite is used as a guide mineral. The masses consist of two distinct types: nonfoliated brown biotite-rich rocks and white biotite-poor rocks. In addition some intermediate varieties occur.

TABLE 1

	1	2	3	4	5	6	7	8
SiO ₂	40.4	50.0	52.1	51.0	39.6	51.1	59.5	62.4
TiO ₂	0.010	0.023	0.010	0.084	1.10	1.10	0.81	0.26
Al ₂ O ₃	0.30	1.85	1.85	1.45	23.8	20.5	17.6	14.0
Fe ₂ O ₃	—	1.34	—	—	1.06	—	—	—
FeO	9.6*	3.48	4.86*	2.64*	8.57	6.36*	4.95*	4.89*
MnO	0.14	0.17	0.16	0.078	0.10	0.041	0.038	0.13
MgO	48.8	36.0	36.0	19.0	5.85	4.50	2.85	4.00
CaO	0.20	1.75	2.35	26.0	8.90	6.20	4.20	9.40
Na ₂ O	0.06	0.10	0.10	0.14	1.70	3.06	4.04	5.60
K ₂ O	0.04	0.10	0.08	nd	4.85	4.00	4.25	2.70
H ₂ O ⁺	—	—	—	—	2.30	—	—	—
H ₂ O ⁻	—	—	—	—	0.14	—	—	—
ZrO ₂	trace	nd	nd	nd	0.074	0.084	0.059	0.028
V ₂ O ₅	nd	0.023	0.017	0.025	0.055	0.033	0.019	0.010
Cr ₂ O ₃	0.030	0.86	0.72	1.10	nd	nd	nd	nd
NiO	0.29	0.12	0.09	0.032	nd	nd	nd	nd
SrO	nd	nd	nd	nd	0.115	0.042	0.031	trace
BaO	trace	0.003	0.001	trace	0.32	0.185	0.195	0.071
Mg/Mg ⁺ Fe	0.90	0.93	0.93	0.93	0.53	0.56	0.51	0.59
Ca/Ca ⁺ Mg ⁺ Fe	—	—	—	—	0.36	0.36	0.35	0.50
Total	100.77	96.75	99.26	102.47	99.42	98.12	99.40	104.58

* FeO calculated from total Fe

** All iron calculated to total Fe for comparison purposes. No correction made for magnetite in rock.

BIOTITE-RICH TYPE

Analysis 5 (table 1) is the average of three analyses of this rock type. The rock consists of about 47 vol. % pleochroic reddish brown biotite (analysis 10, table 1), 2-3 mm across, occurring as clumps or sheaves surrounding gray areas, 3-6 mm across, made up of saussurite consisting of an intimate mixture of untwinned Ab85 ± 2 and low-iron clinozoisite. The oligoclase also is found as larger, clearer grains unmixed with clinozoisite. The calculated mode for the rock is given as no. 5, table 2. Accessories in the rock consist of less than 1 percent zircon, apatite, zoisite, and grossularite with only rare remnants of corroded, twinned calcic plagioclase and augite. Only two grains of calcic plagioclase were found clear enough for U-stage work and, because of poor

TABLE 1

9	10	11	12	13	14	15	16	17	18	19
67.6	32.0	36.4	33.2	65.1	49.0	50.0	35.8	28.9	39.6	41.9
0.23	2.9	3.1	1.34	nd	0.061	0.18	0.004	0.94	trace	0.04
11.2	16.0	16.8	16.8	17.3	0.72	1.46	0.148	15.8	5.58	2.78
—	1.07	—	0.76	—	—	—				
							5.61**	7.63**	2.42**	6.49**
4.83*	16.52	16.60*	11.14	0.039*	14.60*	12.60*				
0.65	0.16	0.19	0.23	trace	1.42	0.34	0.095	0.37	0.29	0.27
3.85	13.2	11.7	21.9	0.10	8.8	9.4	39.4	28.9	37.1	34.8
9.40	0.39	0.88	0.20	0.29	25.5	25.0	0.074	0.68	0.23	0.23
5.93	0.43	0.50	0.20	0.32	0.45	0.89	nd	nd	0.01	nd
2.70	8.80	9.05	9.10	16.10	0.24	0.20	trace	0.02	0.02	0.13
—	2.92	3.00	3.51	—	—	—	12.30	12.60	—	—
	0.18	0.06	0.09	—	—	—	0.42	0.22	—	—
0.059	0.014	0.052	nd	nd	trace	trace	nd	0.16	nd	nd
trace	0.079	0.066	0.031	nd	trace	trace	nd	0.033	nd	nd
nd	nd	trace	nd	trace	nd	nd	0.40	nd	nd	nd
nd	0.020	nd	0.076	nd	nd	trace	0.28	nd	nd	0.086
trace	trace	nd	trace	nd	trace	trace	nd	nd	nd	trace
0.050	0.80	0.27	0.13	0.09	nd	nd	trace	0.004	0.003	trace
0.59	0.57	0.56	0.77	—	0.52	0.57	0.91	0.84	0.95	0.88
0.51	—	—	—	—	—	—	—	—	—	—
107.60	96.05	99.23	99.48	99.34	101.31	100.64	99.44	97.09	86.20	87.60

Analysis

No.	Description
1	Remnant olivine from serpentized peridotite.
2	Remnant orthopyroxene from serpentized peridotite.
3	" " " " " "
4	Clinopyroxene from pyroxenite lens in serpentinite.
5	Biotite-rich acid rock (average of 3).
6	Biotite-poor acid rock with about 30 vol.% biotite and porphyroblasts of albite.
7	Biotite-poor acid rock with about 20 vol.% biotite.
8	Biotite-poor acid rock with only remnant biotite.
9	" " " " " "
10	Biotite from biotite-rich acid rock.
11	Biotite from biotite-poor acid rock.
12	Biotite from dark serpentinite in contact with biotite-rich rock.
13	Microcline from biotite-poor acid rock (average of 2).
14	Diopside from biotite-poor acid rock.
15	" " " " " "
16	Average of nine serpentinite analyses.
17	Dark serpentinite from contact with biotite-rich rock. Sample was biotite-free.
18	Dark serpentinite from contact with biotite-poor rock. Sample was biotite-free.
19	Dark serpentinite from contact with biotite-poor rock. Sample was biotite-free.

orientations, the determinations only indicated the composition was more calcic than Ab40. The rare grains of augite were found contained in biotite. They showed maximum extinction angles of 43° and weak, pinkish pleochroism. They are apparently aluminous augite and are optically quite distinct from the diopside found in lenses in the upper third of the sill (noted earlier). Plate 1-A shows the typical texture of this rock type. It will be noted that the gray saussurite areas surrounded by biotite have a subhedral shape suggesting the morphology of earlier calcic plagioclase. It is in these areas that the remnants of calcic plagioclase are found.

In each biotite-rich mass is found a network of thin veins, usually less than 5 mm wide, principally made up of iron-free zoisite ($\alpha = 1.697$). These veins pinch and swell and are discontinuous. Some portions swell to 1-2 cm and possess lenticular cavities that are filled with anhedral masses of pale pink to colorless anhydrous grossularite grains. Some lenticles are open cavities, the walls of which are lined with large (5-10 mm) dodecahedral crystals of grossularite. Phehnite and margarite are accessories in these veins.

The contacts of the biotite-rich masses with the surrounding serpentinite are always quite sharp. However, biotite flakes are always present in the serpentinite for 3 to 10 inches away from the contact. In addition the serpentinite in this zone is black and dense in contrast to the normal green serpentinite of the sill. Analysis 17, table 1, was made of (biotite-free) serpentinite from the contact. In thin sections it is seen to consist of biotite, stilpnomelane, and some penninite in a matrix of antigorite. The stilpnomelane replaces antigorite and is, in turn, partially to completely replaced by biotite. Composition of biotite from the contact serpentinite is given as analysis 12 (table 1).

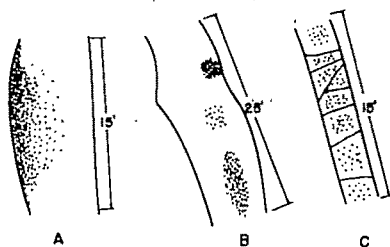


Fig. 2. Sketches of three types of acid rocks classed as intermediate and biotite-poor. A is a composite rock with a high biotite portion grading into a low biotite to biotite-free portion. B has disseminated biotite and "ghost" patches high in biotite. C has only disseminated biotite flakes.

INTERMEDIATE AND BIOTITE-POOR ACID ROCKS

Although the typical biotite-rich rocks consist of between 45 and 50 vol.% biotite, a large number of acid rock lenses in the Jeffrey serpentinite carry from 30 vol.% biotite to practically none at all. These types are illustrated diagrammatically in figure 2. Figure 2A is a composite type with a high biotite portion; 2B carries "ghost"-like high biotite patches; 2C carries only disseminated flakes.

Those which have the larger amounts of biotite appear very much like the biotite-rich bodies except for the presence of white patches, up to 15 mm across, homogeneously scattered throughout the mass. In thin sections the rock

is mineralogically and texturally similar to biotite-rich rocks; however, the white patches consist of porphyroblastic aggregate clusters of clear, twinned, anhedral albite ($Ab\ 91\pm2$). Plate 1-B shows one of these clusters. In addition, close examination of biotite shows that some grains are partially replaced by minute blebs and grains of microcline and diopside. Analysis 6 (table 1) was made of this rock type.

The majority of biotite-poor masses carry less than 10 vol.% biotite as scattered flakes or as patches that appear to be "ghosts" of biotite-rich rocks (fig. 2B). In thin section these rocks are found to consist of microcline (analysis 13, table 1), $Ab\ 95\pm2$, diopside (analyses 14, 15, table 1), and quartz, with accessory sillimanite and muscovite in rare cases. These rocks are usually highly fractured. Biotite flakes are found as accessories only in unfractured portions. Any thin fractures that cut through a biotite patch are bordered by a biotite-free zone of several inches' width on either side (fig. 2C).

These rocks show a tendency to segregate some phases. Pale green diopside is usually mixed with microcline, albite, and quartz but may occur as thin (2 mm) veins. Microcline and/or myrmekitic albite-quartz often occur with quartz and accessory sillimanite as coarse pegmatite patches.

The diopside and microcline are the products of the breakdown of biotite. Plate 1-C shows diopside and microcline replacing biotite as thin slivers or blebs parallel to the mica cleavage. Plate 1-D shows the typical texture of diopside, microcline, and albite in a portion of rock that carries no biotite accessory. In this figure the central diopside grain encloses a small crystal of microcline. The diopside is, in turn, partially enclosed in a larger microcline crystal. This texture is interpreted to be the result of simultaneous crystallization.

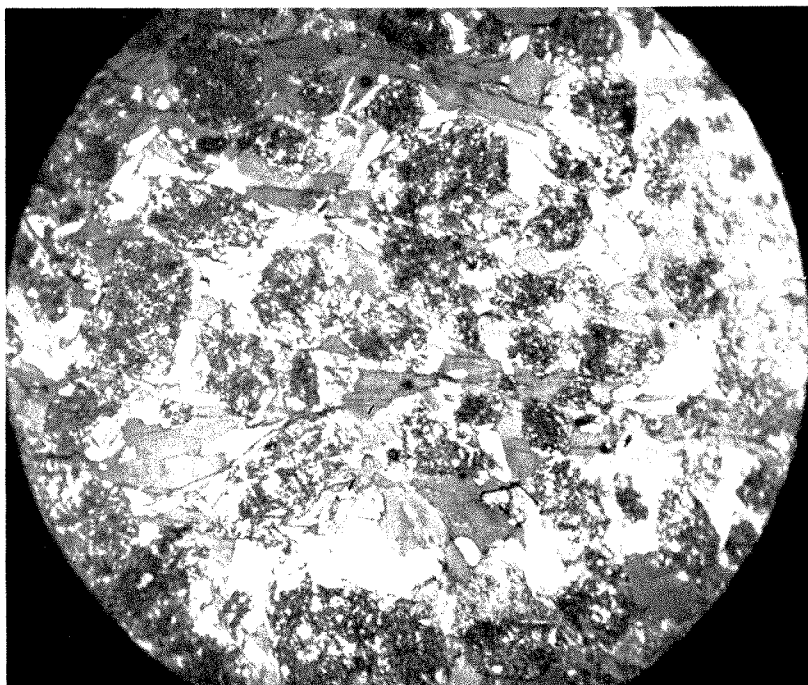
In contrast to the even contacts of the biotite-rich masses against serpentinite, the biotite-poor contacts are ragged and uneven. Feldspar grains with diopside are found contained in the black, dense serpentinite several inches away from the acid rock, or feldspar grains are found jutting out into the contact serpentinite. In addition, serpentinite is found squeezed for several inches into fractures in the acid rock. This ragged contact is interpreted largely as the result of the conversion of biotite (which occurs in the contact zone of serpentinite) to microcline and diopside. In thin sections the contact serpentinite zone for 6-8 inches away from the acid rock is found to consist of biotite flakes, in all stages of replacement by microcline-diopside, and some penninite in a matrix of antigorite. The antigorite is often partially replaced by shreds of talc. Rare biotite flakes show conversion to talc and a dust of magnetite grains. Analyses 18 and 19 (table 1) were made of dark serpentinite from contacts with biotite-poor acid rocks.

Finally it should be noted that in rare instances veins are found in the biotite-poor rocks that consist of fibrous parawollastonite. In a few instances vugs were found that were lined with albite and brushlike fibers of pink pectolite.

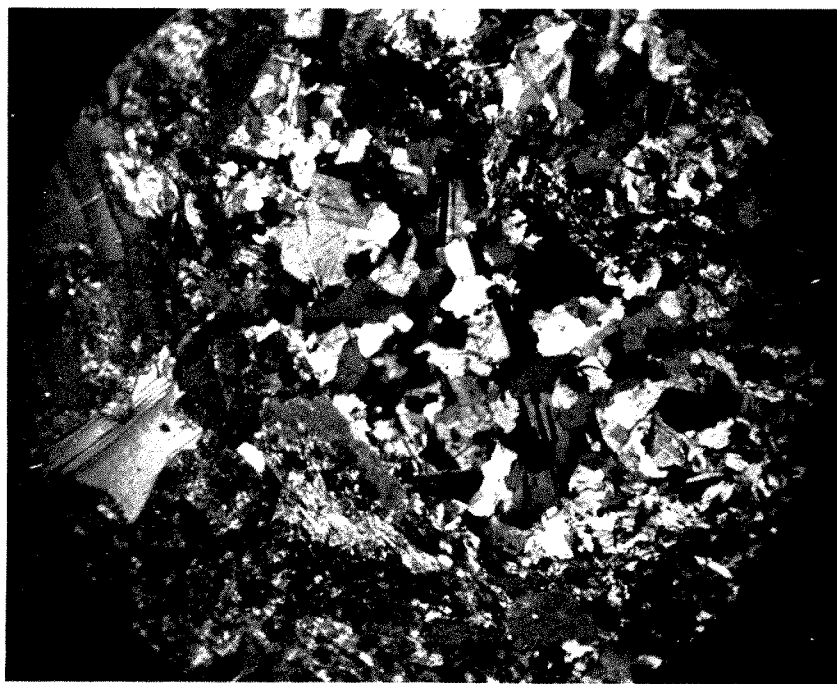
STRUCTURAL FEATURES

Structurally the Jeffrey serpentinite does not possess any consistent mappable elements such as numerous persistent compositional bands or primary S-planes. The lower contact with metasediments strikes approximately N60E and dips 55° SE, while the upper contact strikes about N45E and dips about

PLATE 1



A.

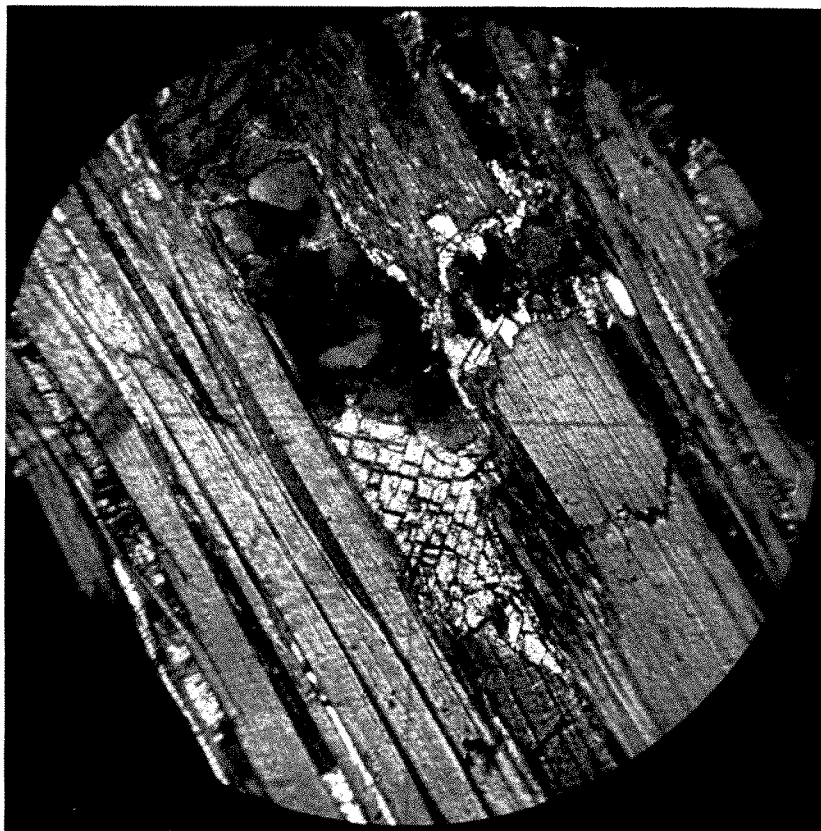


B.

70° SE. The actual map-view distribution of acid rock lenses fortuitously depends on the mining operation and changes from month to month. However, by taking advantage of the lensoid habit of these bodies, it was possible to measure an average dip and strike for each body exposed at a given time. Care was taken not to measure any one body more than once.

The poles to each lens measured were plotted on the *upper hemisphere* of a Schmidt net. To avoid working at the edges of the net it was found to be

PLATE 1



C.

A. Biotite-rich acid rock. Biotite sheaves and oligoclase grains surround areas of saussurite (oligoclase and clinozoisite) that retain the subhedral shapes of original calcic plagioclase crystals. 50x, X Nicols.

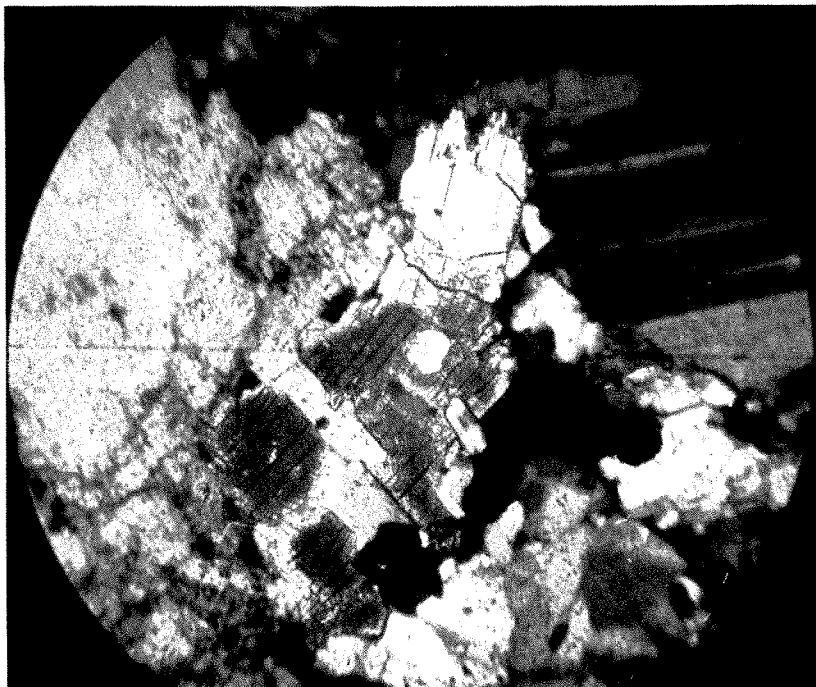
B. Porphyroblastic aggregate cluster of albite crystals in a biotite-rich matrix. The cluster here is about 10 mm. in diameter. The rock is classed as an intermediate type of acid rock. 25x, X Nicols.

C. Diopside (cross-hatched) and microcline (dark gray) replacing biotite. Small blebs of microcline and diopside are developed along other cleavages. 25x, X Nicols.

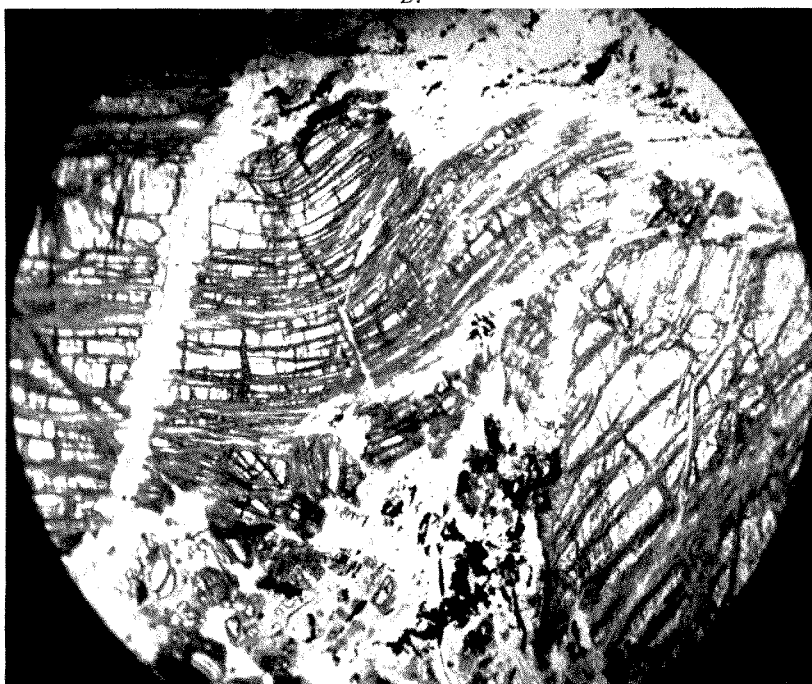
D. Diopside (in center) encloses a small crystal of microcline. Larger microcline crystal partially encloses this diopside grain and another grain of diopside. This texture is interpreted as the result of simultaneous crystallization of diopside and microcline. Twinned albite crystal in upper part of field. 25x, X Nicols.

E. Cataclastic texture of remnant enstatite in serpentinite. 25x, X Nicols.

PLATE 1



D.



E.

much clearer if the sill were "rotated" to a "horizontal" position by the number of degrees of dip of the closest contact. Figures 3A-3E are the plots of all the acid rocks exposed in May 1957, with the sill "rotated" 55° in a direction N30W.

These plots show a strong anisotropy. The twenty-six biotite-rich bodies plot at a strong single peak (fig. 3A), whereas forty-nine biotite-poor bodies plot at two major peaks with a weak partial girdle between them (fig. 3B). When all seventy-five points are plotted together, one weak and one very strong peak result due to the coincidence of the biotite-rich maximum with one of the biotite-poor maxima (fig. 3C). In figure 3D are plotted the poles to thirty-three shear planes in the serpentinite. These show a major peak close to the same maximum of figure 3C.

Figure 3E is a composite drawing of the peak points only, with the planes normal to these peaks drawn in. A and B represent the two acid rock maxima. X and Y are two shear plane maxima. Point Z represents the maximum point of nineteen lineation element measurements. These lie in the plane of shear plane maximum X.

From these data it will be noted that there is a relationship between mineralogy and structural attitude as well as a remarkable symmetry. The acid rocks strike at almost right angles to the sill, and their dips lie symmetrically about 66° apart and about 33° to the pole to the sill (center point of net). Only one of these maxima (A) is approximately coincident with a major shear direction. In the field it was observed that biotite-rich bodies and some biotite-poor bodies were subparallel to shears which sometimes warped around them and sometimes cut them at low angles. However, many biotite-poor bodies were cross-cut by shears which offset the blocks of acid rock. Serpentine is squeezed between the blocks thus separated. Within such acid bodies numerous fractures are developed parallel to the shear planes. As it was noted earlier, these fractures are bordered by biotite-free zones on either side.

INTERPRETATION

Although small acid rock masses are associated with highly serpentinized alpine-type peridotites, similar acid rocks are only rarely associated with unaltered peridotites (MacKenzie, 1960). On the other hand, the association of small olivine-augite gabbro or troctolite masses with unaltered alpine peridotites is common. Guild (1947) described olivine-augite-enstatite-calcic plagioclase lenses in the peridotite of Oriente Province, Cuba. Hadley (1949) in his work on the peridotite of Clay County, North Carolina, found that the body was partially altered to serpentinite and talc schist, and troctolite lenses in it were also partially altered. Olivine is rimmed by enstatite, and bytownite is rimmed by hornblende. These rims are apparently due to deuteric reactions and require the addition of at least water and silica. More highly altered lenses are converted to edenite amphibolites which are associated with veins of sodic plagioclase, corundum, biotite, actinolite, chlorite, and talc. All these minerals cannot be the result of the isochemical alteration of troctolite. They require the metasomatic addition of at least soda, potash, silica, and water.

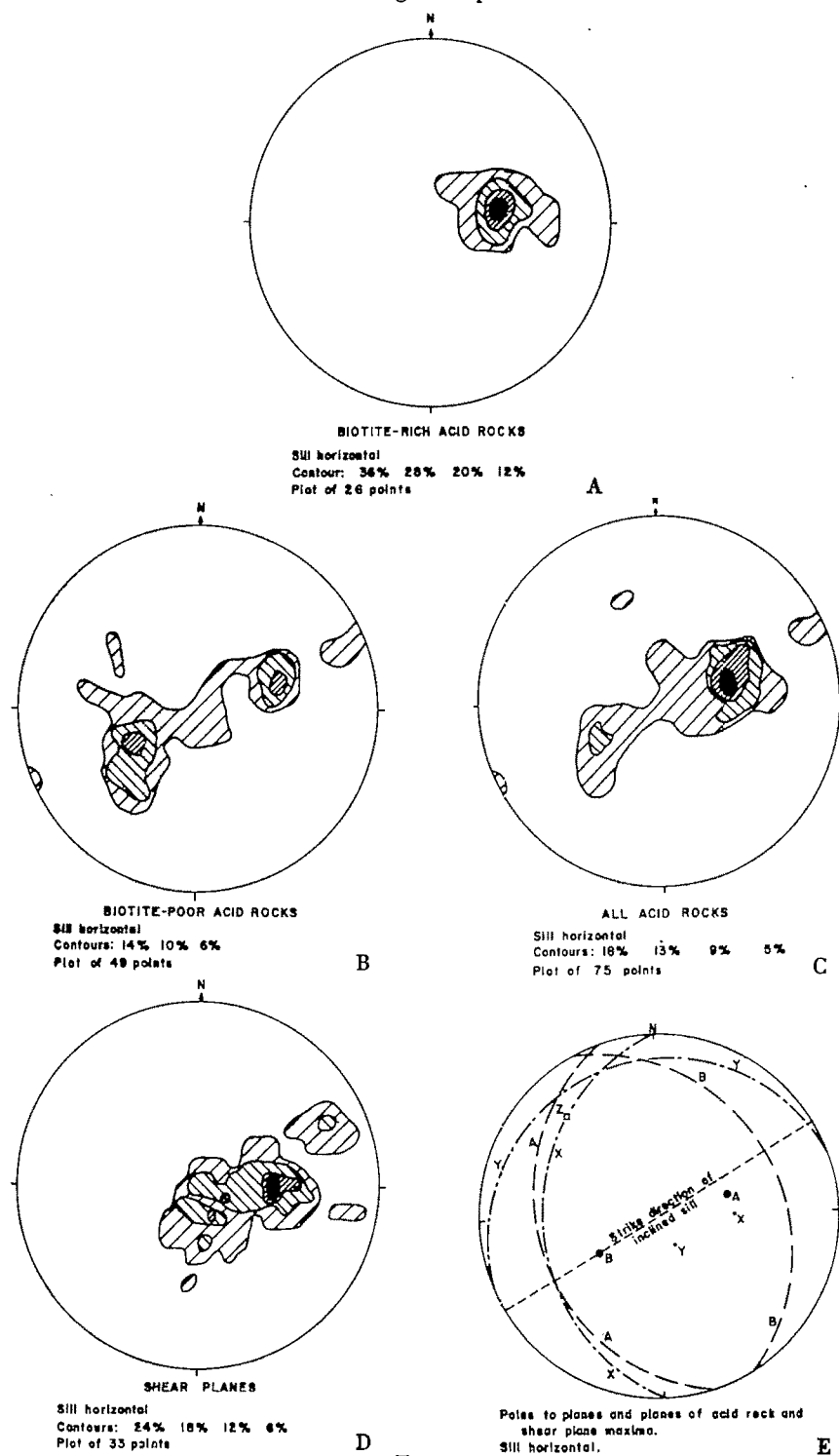


Fig. 3.

In the case of the acid rocks in the Jeffrey sill the remnant minerals, calcic plagioclase and augite, found in the biotite-rich masses strongly suggest that these bodies are metasomatically altered gabbros. The absence of olivine or enstatite remnants does not necessarily mean that they were never present. The original bodies may have been olivine-augite gabbros or simply augite gabbros. The attempt to determine the calcic plagioclase composition optically was unsatisfactory. However, if it is assumed that the present clinozoisite-Ab85 content (no. 5, table 2) is totally the result of the saussuritization of the original calcic plagioclase, the implied composition of the original plagioclase is about Ab30, calcic labradorite. This composition is consistent with the plagioclase compositional range observed in unaltered gabbroic rocks in unaltered peridotites (Guild, 1947). The metasomatic conversion of an original gabbro, of specifically unknown composition, to the biotite-saussurite bodies, now observed, requires, as a conservative estimate, the addition of at least potash and water. It may also have required added silica and alumina. If gabbroic material were removed in great quantity there is no evidence of it in the field. However, it is probable that the accessory veins of zoisite (and grossularite) represent removal and segregation of lime, alumina, and silica from

TABLE 2
Calculated modes from rock analyses

	Mole %	Wt. %	Vol. %
5			
Biotite	42.6	47.6	47.1
Ab 85	26.6	17.6	20.0
Clinozoisite	30.8	34.8	32.9
8			
Microcline	14.3	15.9	17.7
Ab 95	47.0	49.5	53.0
Diopside	37.0	34.2	28.6
Quartz	1.7	0.4	0.4
9			
Microcline	12.5	14.8	16.5
Ab 95	43.6	48.9	52.7
Diopside	34.4	33.9	28.2
Quartz	9.5	2.4	2.4

Fig. 3. A-C represent the plot of poles to lensoid acid rock bodies in the Jeffrey serpentinite. D is the plot of poles to shear planes in the serpentinite. E is a composite plot of maxima points from A-D; the planes normal to each maximum are drawn in. Point Z in E is the maximum of lineation elements found in shear plane X.

All plots are on the upper hemisphere of a Schmidt net. For clarity the plots have been moved 55° in a direction N30W to place the sill in a horizontal attitude and avoid plotting at the edge of the net.

the original gabbro. Analysis 17 (table 1) of the surrounding contact serpentinite shows an enrichment of titanium, iron, manganese, calcium, potassium, zirconium, vanadium, and barium when contrasted with the average of nine normal serpentinite analyses from the Jeffrey pit (analysis 16, table 1). The titanium, iron, manganese, and calcium may have been extracted from the original gabbro. However, the other elements must represent addition from an outside source. Cooke (1937, p. 83) presents a similar analysis of dark serpentinite in contact with an acid rock from Thetford Mines. He contrasts it with an analysis of normal serpentinite, and the same compositional differences are noted as at Jeffrey.

BaO which geochemically follows K_2O is enriched in the biotite of the acid rock (analysis 11), in the contact serpentinite zone, and in the biotite found in the contact serpentinite (analysis 12). This latter biotite has a Mg/Mg+Fe ratio of 0.77 in contrast to the biotite from the adjacent biotite-rich rock where the ratio is 0.57 (analysis 10). This indicates that the two biotites grew in adjustment with two different environments. The Mg to Fe ratio observed in the biotite-rich rock (0.53, analysis 5) indicates the more iron-rich composition of the original gabbro in contrast to the surrounding, highly magnesian peridotite (where the present ratio in serpentinite is 0.91, analysis 16). This difference is to be expected if the gabbros represent a late crystallizing fraction of the original ultramafic mass. Incidentally, it should be noted here that the ratio difference between the biotite of the biotite-rich rock and the whole rock itself is due to a small amount of ferric iron in the clinzoisite of the rock. An approximate calculation indicates less than 5 percent epidote in the clinzoisite.

From the petrographic work described earlier, it was possible to follow a sequence of changes in these acid bodies whereby more sodic plagioclase appeared, clinzoisite disappeared, biotite showed decomposition to microcline and diopside, and silica appeared in excess as quartz. In addition some fairly rare specimens showed a small excess of alumina as sillimanite. Analyses 5 through 9 (table 1) represent a sequence of acid bodies with decreasing visible biotite content. From optical estimates, analyses of rocks, and from analyses of microcline, biotite, and diopside it was possible to calculate approximate modes for rocks 5, 8, and 9 (table 2).

On the basis of the petrographic work it is concluded that the intermediate and biotite-poor bodies represent further alteration of the biotite-rich rock type. Figures 4 and 5 are simple variation diagrams on the basis of increasing SiO_2 going from rock 5 to rock 9 (left to right). The ratio of Mg/Mg+Fe in figure 3 varies from 0.53 to 0.59, rising to the latter value in almost biotite-free rocks 8 and 9. The variation in this ratio indicates a small enrichment in Mg or the removal of some Fe under the conditions of final alteration. In figure 4, Al_2O_3 , FeO and TiO_2 drop through the sequence while Na_2O rises. K_2O shows only a small variation in higher biotite rocks 5, 6, and 7, and then drops in the low biotite rocks 8 and 9. MgO drops slightly through 5-6-7 and then rises slightly in 8 and 9. CaO drops steadily in the higher biotite rocks and rises sharply in low biotite rocks. Through the sequence of rocks which carry significant amounts of biotite (5-7), the CaO content is independent of

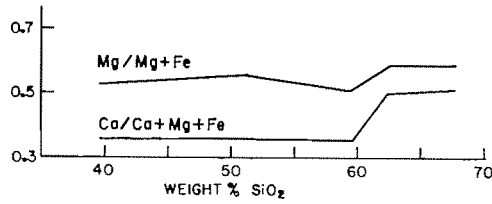


Fig. 4. Variation of ratios $Mg/Mg + Fe$ and $Ca/Ca + Mg + Fe$ against $\%SiO_2$. The variation is taken from acid rocks showing decrease in visible biotite content (going from left to right, analyses 5-9, table 1.).

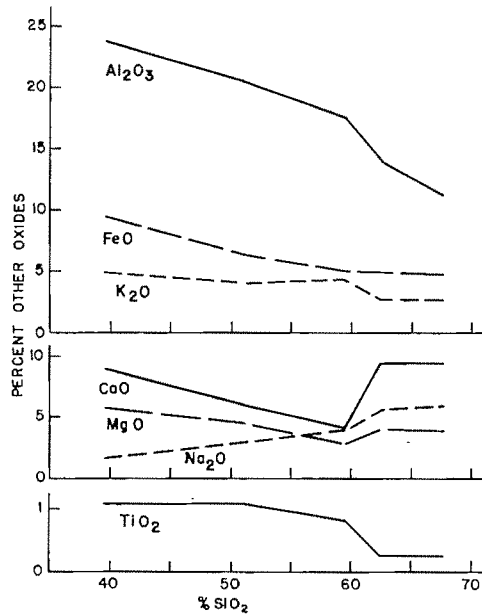


Fig. 5. Oxide variation plotted against $\%SiO_2$ for acid rocks with decreasing visible biotite content (going from left to right, analyses 5-9, table 1.).

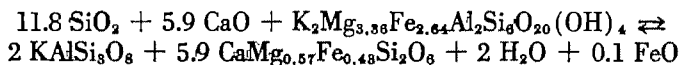
Mg. However, there is a slight relationship between calcium and iron in the small epidote content of the clinozoisite of these rocks. This is small enough that CaO may be considered relatively independent of both Mg and Fe in the rocks in which biotite is stable. However, in the low-biotite to biotite-free rocks, 8 and 9, Ca is largely dependent on Mg and Fe in the diopside which replaces biotite as the major ferromagnesian mineral. The variation of the ratio $Ca/Ca + Mg + Fe$ exhibits a more regular trend through the sequence of rock types than does the simple variation of CaO. In figure 4 this ratio shows little variation through the sequence of higher-biotite rocks 5, 6, and 7, and then jumps to a steady higher value in biotite-poor rocks 8 and 9. The jump apparently reflects the dependence of Ca on Mg and Fe and also suggests an introduction of Ca into these rocks thereby making biotite unstable (discussed below).

The most conservative interpretation that can be made of the data is that the alteration of the biotite-saussurite assemblage to the final diopside-micro-

cline-albite-quartz assemblage is the result of major additions of silica, lime, and soda, and obviously the loss of water. The dropping percentages of other oxides are due in part to relative dilution. Iron may have been removed in small amounts and small amounts of magnesium may have been added. Evidence is given below which indicates that potash remained fairly constant and that its drop-off in the variation diagram is due almost entirely to the dilution effect of added material.

The breakdown of biotite to microcline and diopside is of particular interest in that diopside is not the usual ferromagnesian mineral found in serpentinite-acid rock associations. The only other place in the region where diopside is significant is in the acid bodies associated with serpentinite at the Montreal Chrome Pit about seven miles southeast of Thetford Mines (Cooke, 1937, p. 79). At Thetford Mines itself, actinolite is the common mafic mineral (Cooke, 1937, p. 81), and in other occurrences around the world hornblende is often found in this type of rock. The absence of hornblende at Jeffrey is attributed to low available alumina. On the other hand, actinolite is not stable in the higher temperature amphibolite facies which the biotite-poor acid rocks represent (discussed below). This is apparently also the reason why diopside pyroxenites in the upper third of the sill have not been altered to actinolite amphibolites.

The conversion of biotite to diopside-microcline is a critical reaction in going from the epidote-amphibolite to amphibolite facies (Ramberg, 1952). The reaction requires both available lime and silica. Biotite (phlogopite) is often stabilized in amphibolite facies marbles because of low available silica in a highly calcic environment (Ramberg, 1952, p. 152). An idealized reaction would be:



In this reaction a simplified biotite with a Mg to Fe ratio of 0.56 is converted to a diopside with a ratio of 0.57. These ratios correspond to the ratios determined in unreacted biotite (analysis 11, table 1) which was found coexisting with diopside (analysis 15) in a biotite-poor acid rock. A small release of iron occurs on the right-hand side. Ramberg (1952, p. 152) pointed out that in amphibolite facies carbonate rocks the Mg to Fe ratio is usually somewhat higher in diopside than in coexisting biotite. It is interesting to note that the idealized reaction predicts a diopside to microcline molar ratio of 2.95:1 in the product. Calculated modes for rocks 8 and 9 (table 2) give molar ratios of 2.6 and 2.8:1, respectively. This suggests that the K₂O content of the rock remained fairly constant during the alteration, and the drop observed in the variation diagram is due largely to relative dilution.

The association of diopside with sodic plagioclase led Tilley (1927) to assume that diopside was stable in the low epidote-amphibolite facies. Ramberg (1952) pointed out that the plagioclase composition is a response to bulk composition and that diopside is always indicative of the amphibolite facies. The presence of accessory sillimanite in some of the biotite-poor acid rocks further confirms amphibolite facies conditions.

The structural data presented earlier suggest that the original gabbro masses lay in two major orientations 66° apart. One group may have been in an attitude which corresponded with an original strong joint system whereas the other set lay in a complementary set of weaker joints. In this regard Guild (1947) noted the presence of two dominant joint sets in the peridotite of Oriente Province, Cuba. The poles to these joints plotted at two strong maxima about 80° apart. A plot of the poles to lenticular olivine gabbro bodies showed two maxima, about 25° apart, one of them corresponding to one of the joint maxima. The similarity of the two cases is striking.

During subsequent deformation, possibly accompanying serpentinization, the strongest set of joints would most likely be utilized as a shear direction, and the shear planes would act as zones of entry or localization of introduced material. Under the initial P-T conditions (possibly high epidote-amphibolite facies) the gabbros were altered to the biotite-saussurite assemblage by reaction with introduced potash and water. Increasing metamorphism moved into the amphibolite facies field and the introduced material became largely soda, lime, and silica rich. The acid bodies which lay transverse to the major shear direction were most thoroughly altered by the new material. They were cross-faulted and cross-jointed, and biotite persisted as unreacted remnants only in portions that were unfractured.

CONCLUSIONS

Ramberg (1952, p. 156) places the upper limit of the amphibolite facies at about 400°C . A pure magnesian serpentinite is stable to 500°C (Bowen and Tuttle, 1949). Thus, serpentinites are not diagnostic of the particular facies of metamorphism under which they formed. The mineralogy of the hydrothermally altered gabbros of the Jeffrey sill indicates amphibolite facies conditions were attained at some time in the history of the whole mass. The very weak contact metamorphic effect along the footwall indicates hornfels development also in the amphibolite facies. On the other hand, the surrounding country rocks represent adjustment only to epidote-amphibolite facies conditions. Thus, the serpentinite and its associated acid rocks are regionally out of grade with the country rocks. This disparity may be interpreted in several ways.

(1) The peridotite sill was intruded as a relatively cool mass which resulted in only a very weak hornfels development at the contact. During subsequent deformation, the sill, lying in a plane of weakness, acted as a locus for deformation and an avenue for the introduction of added components and water.

(2) The peridotite sill was first intruded at greater depth than is represented by the country rocks which now surround it. It was serpentinized (and the gabbros altered) at a depth commensurate with an amphibolite facies level of metamorphism. The plastic serpentinite, with its acid bodies, was subsequently moved as a solid into the higher level (and lower grade) country rocks in which it is now found. The heat loss was lower than the rate of movement so that the serpentinite was slightly hotter than these rocks and a small contact hornfels zone developed.

MacKenzie (1960) found a strong amphibolite facies hornfels development associated with the intrusion of the virtually unserpentinized Tinaquillo peridotite in Venezuela. Here again the country rocks are in the epidote-amphibolite facies. On the basis of this single case one is inclined to favor the second alternative suggested above.

On a broader regional basis, if one assumes that the serpentinites of the Eastern Quebec belt are more or less contemporaneous within short distances, then the Jeffrey body must have a history similar to the well-studied body at Thetford Mines (Cooke, 1937). At Thetford Mines there is no contact hornfels development, and the acid rocks carry actinolite, tremolite, and epidote which represent the epidote-amphibolite facies. The country rocks are also in the same facies. However, at the Montreal Chrome Pit, just seven miles southeast of Thetford Mines, diopside occurs in acid bodies and the level of metamorphism is higher. A detailed study of the region as a whole was not made by the writer but one significant observation can be made. According to Cooke's maps (1937), the serpentinite at Thetford Mines and the belt to the southwest of it lie on the crest of a regional anticlinal structure. But, at the Montreal Chrome Pit and at the Jeffrey Mine the serpentinites lie on the flanks of the same fold. It is possible that the flanking position suffered more intense deformation and development of higher temperatures than the crestal position, and thus was created a sharp P-T gradient across the structure which resulted in facies changes in relatively short distances. This would also account for the fact that the supposed original attitudes of the gabbro bodies at Jeffrey were only partially destroyed by subsequent deformation. That is, a weak partial girdle was developed during deformation by the rotation of some bodies, but the strong original maxima were not totally destroyed as they would have been had the whole serpentinite mass been remobilized and moved to shallower depths as is implied by the second alternative presented above.

Little can be said concerning the source of the components which effected the alteration of the gabbroic rocks in the Jeffrey sill. For that matter the alteration cannot be dated definitely as pre- or post-serpentinization, or synchronous with it. However, by comparing analyses 1, 2, and 3 of primary olivine and enstatite with analysis 16 (the average of 9 serpentinites), it will be noted that the small amounts of potash, soda, and lime found in the primary minerals are virtually absent in the serpentinite. For example, an approximate calculation shows that if the original peridotite consisted of 90 vol.% olivine (analysis 1) and 10 vol.% enstatite (analyses 2 and 3 with an average of 2% CaO) and was thoroughly converted to serpentine and magnetite, the serpentinite rock should carry about 0.3% CaO in the analysis. Analysis 16, of serpentinite, shows only 0.07% CaO, or less than one-fourth of the expected amount. This discrepancy is larger than would result from an analytical error of as much as 15%. On this basis it would appear that the alteration of gabbros accompanied serpentinization and resulted, at least in part, from oxides released during the process.

CHEMICAL ANALYSES

All chemical analyses were made by the writer at the Spectrochemical Laboratory of the Department of Geology, University of Chicago. Metals were determined spectrographically. Alkalies were determined (flame) photometrically against N.B.S. standards. Ferrous iron was determined by titration against standardized ceric solution. Constituent water was determined by the Penfield method.

In table 1 a dash (—) indicates that the oxide was not sought. The letters "nd" indicate the oxide was not detected within detection limits (usually 10 ppm $\pm$). The observed analytical error is 2% for alkalies and 1% for ferrous iron. For spectrographically determined elements the expected error is 10% at least. In the work performed here, unknowns were arced alternately with knowns (such as G-1, W-1) which were diluted to bracket the percentage of the oxide sought in the unknown. Thus a working curve was re-established on each plate in the percentage range sought. Replicate arcings of knowns yielded observed variations within 7.5%. Thus, 10% may be safely used as the maximum error.

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DIABASIC AND GABBROIC INTRUSIONS IN THE FROST MOUNTAIN AREA, SOUTH-CENTRAL CASCADE MOUNTAINS, WASHINGTON

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ABSTRACT. Diabasic and gabbroic intrusions in the Frost Mountain area of the south-central Cascade Mountains of Washington, approximately 70 miles southeast of Seattle, represent at least in part feeders for two different sets of basalt flows. The older Naches basalt flows are probably Eocene in age, and the younger Yakima basalt flows are Mio-Pliocene. Field relations are of prime importance in distinguishing the two generations of intrusive bodies, but it is also generally possible to separate them by differences in degree of alteration.

INTRODUCTION

The Frost Mountain area is in the south-central Cascade Mountains of Washington, approximately 40 miles northeast of Mount Rainier and 70 miles southeast of Seattle (fig. 1). In this area, there are two sequences of basalt flows, the older probably Eocene in age and the younger Mio-Pliocene. Connections between the flows and intrusive bodies indicate that both sequences were fed locally. The two generations of intrusions are similar in texture and mineral composition, but usually can be distinguished by degree of alteration; the older are notably more altered than the younger.

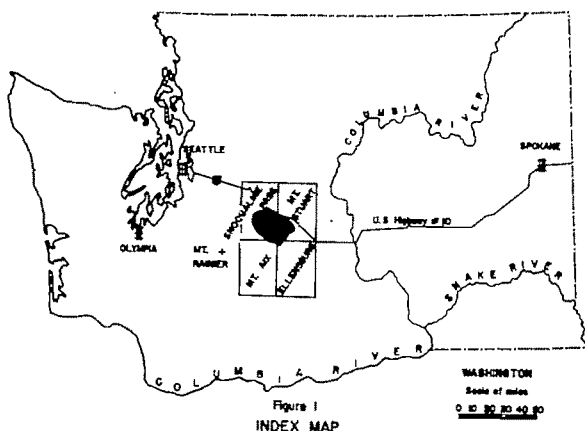
Geologic setting.—Pre-Tertiary igneous and metamorphic rocks make up most of the northern and central Cascade Mountains in Washington, forming a "basement complex" in the Frost Mountain area. The basalt flows of the older generation are interbedded with the sedimentary and volcanic rocks of the Naches formation, generally considered to be Eocene in age (Smith and Calkins, 1906; Stout, 1959). The Naches formation is overlain unconformably by a thick pile of Oligo-Miocene (?) andesitic rocks probably correlative with the "Keechelus formation" as redefined by Foster (1960, p. 118-121). The younger basalt flows rest unconformably on the Keechelus andesites and are continuous to the east with the Yakima basalts, of probable Mio-Pliocene age (Waters, 1955). A description of the areal geology of the Frost Mountain area is currently being prepared for publication.

The term "Keechelus" is used here merely for convenience in referring to the entire stratigraphic section of Oligo-Miocene (?) andesitic rocks in the Frost Mountain area. At present, there is confusion as to exactly what the "Keechelus formation" represents because of the difficulty in correlating the volcanic units at the type locality with those elsewhere.

FIELD RELATIONS

Naches flows and intrusions.—The Naches basalt flows (1) are interbedded with arkosic sandstones and conglomerates and/or rhyolitic rocks; (2) usually have been deformed—some flows are now vertical or overturned; (3) are commonly amygdaloidal or megaporphyritic and/or highly vesicular; (4) are commonly altered.

Diabasic and gabbroic intrusions of the older generation are at least in part feeders for some of the Naches flows. Two intrusions near Mount Clifty



(fig. 2) can be traced almost continuously into basalt flows of the Naches formation.

Yakima basalt and intrusions.—The Yakima basalt (1) characteristically forms large talus slopes, sometimes more than a square mile in total area; (2) is found predominantly as ridge-cappings; (3) is usually very fresh; (4) commonly has columnar structure and blocky fractures; (5) rarely has amygdaloidal and megaporphyritic textures.

The younger diabasic and gabbroic intrusions commonly cut andesitic rocks tentatively correlated with the Keechelus formation. The intrusions range in size from small dikes less than 1 foot thick to large, pluglike bodies cropping out over more than a square mile. Most of the younger intrusions have a pronounced northwesterly trend, probably reflecting control by “basement” structures. They occur principally between the two belts of pre-Tertiary rocks (fig. 2).

In at least three places, diabasic and gabbroic intrusions of the younger generation can be traced into flows of Yakima basalt, but exposures are so poor that the actual connections of “dikes” and flows are rarely seen.

Just west of Frost Mountain a flow of Yakima basalt caps a small peak, and directly below it, to the north, are good exposures of a large diabasic body which partly intrudes Keechelus (?) rocks. A traverse on the northern ridge shows diabase grading into basalt in a distance of less than 100 feet.

Approximately $2\frac{1}{2}$ miles northeast of Frost Mountain, a large, basic intrusion seems to connect with the lower flows of Yakima basalt, but talus and soil cover the contact. Approximately $1\frac{1}{2}$ miles to the southeast, a smaller diabasic body is in contact with Yakima basalt, but again the contact is unexposed.

Smith (1904, p. 8) reported a diabase dike cutting the lower flows of Yakima basalt in the southeastern part of the Frost Mountain area. He stated:

“The largest of these dikes occurs on the west side of North Fork of Mamastash Creek and is unique in that it cuts the lower sheets of Yakima basalt. This occurrence, together with the general distribution of the diabase, justifies the conclusion that the diabase originated from the same magma as the Yakima basalt, the larger masses of diabase representing

the intrusive bodies of molten rock which connected upward, through conduits now indicated by the dikes, with the lava flows at the surface". The only dike that could be found near this locality intrudes Keechelus volcanic rocks and not Yakima basalt.

COMPARATIVE PETROLOGY

Basic intrusions of both generations are extremely friable, and exposures are rounded by weathering. Plagioclase laths and pyroxene can readily be identified in most specimens, and some rocks contain glomerophyric clusters of pyroxene that produce a spotted appearance.

Feeders of both generations have similar mineral compositions: plagioclase (45-60%), pyroxene (20-35%), and opaques (3-10%). The textures are usually ophitic to subophitic. No diktytaxitic textures were found. Zoned plagioclase is rare. The pyroxene is predominantly pigeonite, much of which is uniaxial or has a very small optic angle ($2V_x = <15^\circ$). Much of the pigeonite may be titaniferous, judging by its light-brown pleochroism.

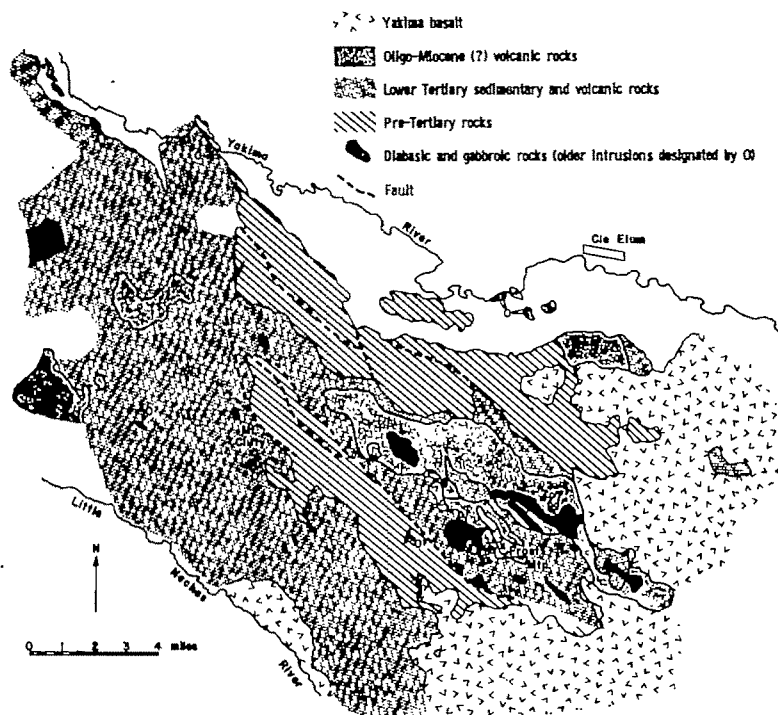
Although the feeders of the two generations have similar textures and mineral compositions, the following petrographic characteristics, considered collectively, can generally be used to separate the younger from the older ones:

<i>Younger rocks</i>	<i>Older rocks</i>
Olivine is common and may be partly altered.	Olivine, if ever present, has been completely altered.
Glass may be present.	Glass is not present.
Quartz is rare.	Quartz is common.
Pyroxene is generally fresh.	Pyroxene is partly or completely altered.
Plagioclase may be fresh or altered and has a compositional range of An_{55} to An_{87} .	Plagioclase is commonly altered and may be more calcic (An_{60} - An_{76}).
No albitization.	May be partially albitized.

Alteration in the older intrusions is manifested by saussuritized and/or kaolinized plagioclase and chloritized pyroxene. Much of the plagioclase has been replaced by calcite. The groundmass consists of chloritic material, chlorophaseite, and other alteration products. In a few thin sections, the pyroxene is relatively fresh, although the plagioclase is altered. Quartz may form as much as 5 percent of the rock, and much of it is resorbed.

A striking property of some of the younger basic intrusions is kaolinization and/or saussuritization of the plagioclase with no or very little alteration of the pyroxene. Degree of alteration does not seem to be affected by grain size. Alteration may be localized, especially where the rocks have been fractured or faulted. Local alteration is also shown in almost vertical, light- and dark-colored flow layers in the relatively large, diabasic intrusion about $1\frac{1}{2}$ miles west of Frost Mountain. The light-colored layers contain completely kaolinized plagioclase, some zeolites, and relatively unaltered pigeonite, but the dark layers contain relatively fresh plagioclase and unaltered pigeonite. Magnetite occurs as small, blocky crystals in the dark layers and as large, skeletal crystals in the light-colored layers. The dark layers are more typical of the average Yakima basalt feeder.

Figure 2
GENERALIZED GEOLOGIC MAP SHOWING DISTRIBUTION
OF DIABASIC AND GABBROIC ROCKS



The highest olivine content in the younger intrusive rocks, up to 10 percent, is in the large, westernmost body (fig. 2). Smaller amounts of olivine are more common in the intrusions, and not all intrusive bodies contain olivine. The olivine is partly altered to iddingsite, saponite and/or other chloritic or clay materials.

The largest amount of olivine in the Yakima basalt flows in the Frost Mountain area, 5 to 8 percent, is in the flows on Frost Mountain. Smaller amounts are common in other flows of Yakima basalt. The large, olivine-rich intrusion to the west is a possible feeder for flows having a relatively high olivine content.

Olivine-rich basalts are not uncommon on the Columbia Plateau, although they seem to be confined to the upper part of the Yakima basalt. The writer examined about 50 thin sections from flows near Vantage, Washington, in the west-central part of the Columbia Plateau. The Roza porphyritic flow (Laval, 1956) contains up to 8 percent olivine, although the average olivine content in this and other flows, including the Priest Rapids flows (Laval, 1956), is generally less than 5 percent. The locations of the samples within the flows are not known, and this factor is critical before attempting correlation on this basis. The Wenas basalt exposed in the Ellensburg quadrangle and vicinity also has a rather high olivine content (Smith, 1903; Laval, 1956); it pinches out to the east (Waters, 1955, p. 673).

Detailed study of basalt stratigraphy between the Frost Mountain area and the Ellensburg and Yakima River districts to the east has not been undertaken, so that no definite correlations can yet be made. Exactly how many and what flows came from the west is not known.

TEANAWAY DIKE SWARM

A somewhat similar problem involving two different generations of intrusions is apparently presented by the Teanaway dike swarm which crops out in an elongate, east-west trending belt, approximately 15 miles north of Cle Elum. Chappell (1936a, p. 156; 1936b, p. 384) reported a multiple dike in the Wenatchee quadrangle, east of the main part of the Teanaway dike swarm, and explained the different stages of intrusion as representing feeders for both the Eocene Teanaway basalt and the Mio-Pliocene Yakima basalt. He noted that the older dike was coarser grained and more altered. Chappell also noted that foreset bedding in palagonitic breccias within the Yakima basalt in the Wenatchee area indicated that one or more flows came from the west or southwest.

Approximately 150 thin sections representing 46 different dikes in the Teanaway dike swarm were examined. The writer did not visit the individual localities, however, so that the field relations are unknown. Using the petrographic characteristics listed earlier to differentiate the two generations of intrusions in the Frost Mountain area, the thin sections of the Teanaway dikes can be divided into two groups: (1) those with pronounced alteration of plagioclase, groundmass material, and pyroxene, with no olivine, and (2) those which are relatively fresh and sometimes contain olivine. On this basis, it appears that the Teanaway swarm, especially in its easternmost part, includes dikes of two generations.

ACKNOWLEDGMENTS

Appreciation is extended to H. A. Coombs and J. H. Mackin, University of Washington, for allowing the writer to examine their collections of thin sections of the Teanaway dike swarm and the Yakima basalt, and for their suggestions and critical comments.

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VARIATION IN COMPOSITION OF BIOTITE AND ACTINOLITE FROM MONOMINERALIC CONTACT BANDS NEAR WESTFIELD, MASSACHUSETTS

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ABSTRACT. Serpentine occurs near Westfield, Massachusetts associated with amphibolite and impure marble in several thin lenses intercalated in steeply dipping pelitic schist. The schist and lens rocks are intimately intruded by quartz diorite. Where the quartz diorite has intruded serpentine or marble, thin monomineralic bands of biotite and actinolite have developed parallel to the contact, with the biotite band next to the intrusive.

Twelve biotite and seven actinolite samples from one area of the monomineralic banding have been analyzed in duplicate by rapid analysis methods. The standards G-1, W-1, and Haplogranite were analyzed at the same time and under the same conditions. The ranges of variation of the major element concentrations in the biotites are SiO_2 : 37.93–42.05%; Al_2O_3 : 14.26–19.22%; FeO : 2.90–7.96%; Fe_2O_3 : 1.13–3.04%; MgO : 17.98–24.42%; and K_2O : 8.96–10.31%. In the actinolites the ranges are SiO_2 : 51.33–58.34%; Al_2O_3 : .02–7.70%; FeO : 2.28–3.90%; Fe_2O_3 : .56–1.74%; MgO : 19.49–24.90%; and CaO : 10.04–13.34%.

Results from analyses of biotite-actinolite pairs taken at varying distances from the contact between the two bands indicate culminations and depressions perpendicular to the contact in the content of the various elements of the two minerals. The variations in the $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios in the two minerals indicate a degree of chemical disequilibrium in the bands, as it can be shown that attainment of equilibrium requires that the $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios in different samples of the same mineral be similar.

INTRODUCTION

Purpose.—Petrographic studies of mineral and rock associations found at serpentine and marble contacts have often been carried out. Bulk chemical analyses have likewise been made in many instances. Little is known, however, about the variation in composition of coexisting contact minerals. This study provides a quantitative idea of the amount of mineral compositional variation in monomineralic biotite and actinolite bands found paralleling the contact of serpentine-marble with intrusive quartz diorite. Among the samples analyzed are five pairs of coexisting biotite-actinolite, taken at different distances from the contact between the two bands. The analyses of these pairs give an indication of the direction of movement of the various elements and of the relation of the composition of the minerals to distance from the contact. Utilizing the chemical results, a method is presented here for testing the degree of attainment of thermodynamic equilibrium in such bands. This work is also an example of the precision and accuracy of rapid analysis procedures as applied to minerals, as all samples were analyzed in duplicate and the standards G-1, W-1, and Haplogranite were run at the same time and under the same conditions.

Previous work.—Monomineralic banding at the contacts of serpentine bodies is well known. Phillips and Hess (1936) discuss contact effects between serpentine and siliceous country rocks as shown in the northern Appalachians. Two main types are distinguished: (1) the low-temperature type is marked by formation of a band of chlorite at the edge of the country rock schist and of talc at the edge of the serpentine; (2) the high-temperature type has a band of biotite at the edge of the country rock and of actinolite at the edge of the ser-

pentinite. The same contact minerals have been reported by numerous other investigators. A particularly interesting case is described by Read (1934), who studied small round bodies of rock from the Shetland Islands that are made up of circular monomineralic zones. The zoning tends towards the following ideal sequence from the center outwards: antigorite, talc, actinolite, chlorite, biotite, country rock. Only seven analyses of actual contact specimens of biotite and one of actinolite could be found in the literature (table 3). The occurrence of many analyzed samples reported as "contact" specimens is inadequately described. Most of them appear to be from metamorphosed carbonate rocks in the vicinity of igneous contacts.

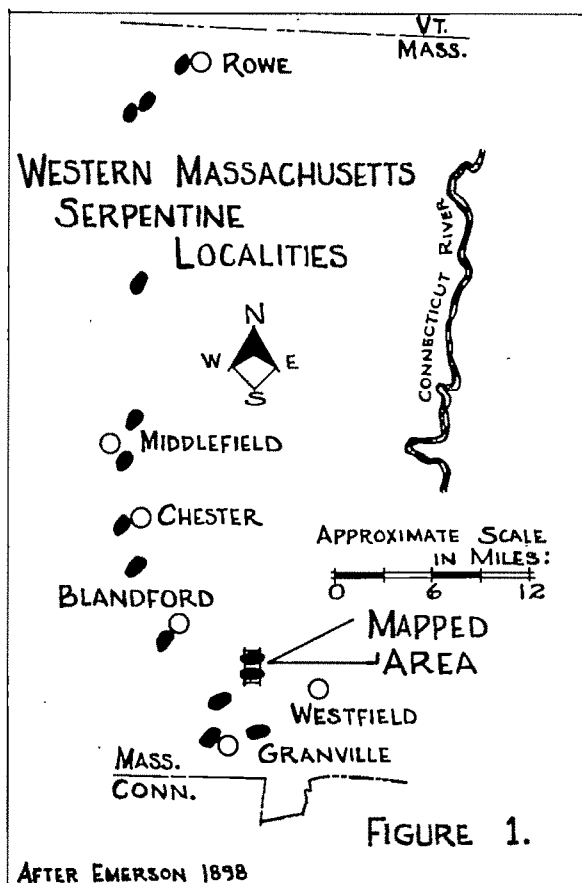
In recent years the variation in composition of biotite and of the amphiboles has received increasing attention. Hall (1941) discusses the relation between color and composition in biotites, and presents 56 analyses of biotites for MgO , FeO , TiO_2 , and Fe_2O_3 , mostly taken from the literature up to 1941. Heinrich (1946) gives 17 analyses of biotites representing the maximum content of the various constituents which may occur in the mineral. Hallimond (1943) presents 196 analyses from the literature in a graphical study of chemical variation in the calciferous amphiboles. A recent summary of present knowledge of chemical variation in natural amphiboles has been given by Boyd (1959).

GENERAL GEOLOGY

Area mapped.—During 1957 and 1958 an area of about two square miles was mapped in detail in the serpentine belt of western Massachusetts. The area, consisting of two abandoned serpentine quarries and the immediately surrounding rocks, is on the western edge of the Connecticut Valley, about eleven miles west of Springfield and about four miles west of Westfield. The serpentine occurrences are part of the Massachusetts section of the eastern North America serpentine belt (fig. 1). A descriptive study of the serpentine area can be found in Emerson (1898).

Field relations.—Most of the area is made up of pelitic schist and coarse-grained quartz diorite. The schist has the texture and mineralogy of a typical high-grade pelitic schist. Porphyroblasts of kyanite and garnet occur in a fine-grained schistose groundmass of biotite, muscovite, oligoclase, quartz, and magnetite. The dip of the schist varies from vertical to 60° east or west, and is gently warped, varying in strike from N25E to N25W. Everywhere quartz diorite intrudes the schist as large separate masses and as small intimate veins and small masses which appear to grade into the schist. Throughout the area the quartz diorite apparently consists only of quartz, muscovite, and oligoclase, with rare apatite or beryl.

Along a north-south line through the quarries several thin lenses composed of varying combinations of serpentine, amphibolite, and impure marble are intercalated in the schist. These vary in thickness from a few inches to 500 feet and in length from 6 inches to $\frac{3}{4}$ mile. They are also intruded by quartz diorite. The amphibolite and marble are banded and schistose. The serpentine is sometimes banded and schistose. The strike of the lenses agrees with that of the enclosing schist, which wraps around the ends of the larger lenses.



The lenses, which are restricted to a thin zone about 1000 feet wide, in places exhibit nearly complete textural and mineralogical gradations between amphibolite, serpentinite, and impure marble. In the vicinity of the northern quarry the amphibolite varies from a banded quartz-actinolitic hornblende-andesine rock through chlorite- and epidote-bearing rocks to massive serpentinite with lesser carbonate and talc. At the southern quarry banded actinolitic marble passes directly into banded serpentinite. Thin sections from these rocks exhibit all degrees of replacement of tremolite-actinolite by antigorite, often in association with carbonate. In addition, medium-grained to coarse-grained masses of forsterite show strong replacement by these minerals. Diopside-actinolitic hornblende-epidote-calcite-biotite rock is found south of the southern quarry. Smaller lenses in the area show various gradations between the quartz-bearing amphibolite and actinolitic hornblende-epidote-andesine amphibolite. Details of the field and petrographic work may be found elsewhere (Brownlow, 1960).

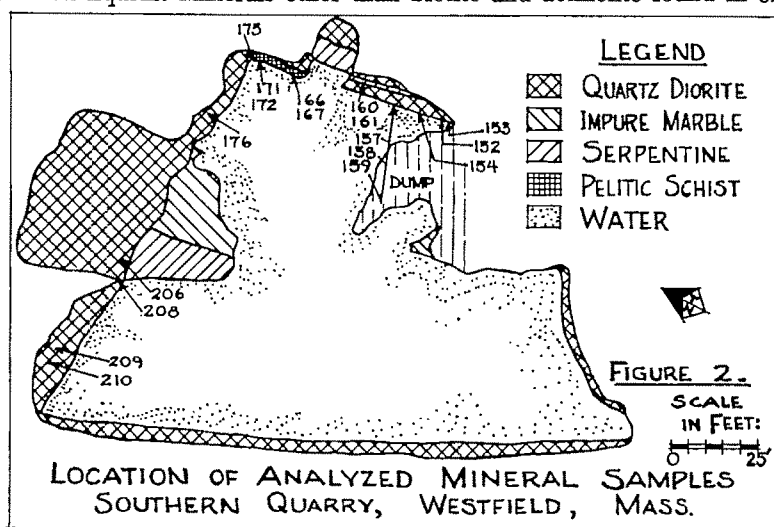
Monomineralic banding.—Where the quartz diorite has intruded serpentinite or marble, thin monomineralic bands of mica and actinolite have de-

veloped parallel to the contact. These vary from less than an inch to one foot in width, with the actinolite next to the marble or serpentine and the biotite next to the quartz diorite. All contacts are generally sharp. Either or both of the contact minerals may grow perpendicular to a particular contact. At one small area at the southern quarry similar banding is found between schist and serpentine-marble. No other contact effects are visible in the marble, but talc has often developed in the serpentine. In places abundant black tourmaline occurs in the quartz diorite next to the biotite band. Adjacent to the biotite band the quartz diorite is more or less fine grained but grades rapidly to its normal coarse grain within a few inches to one foot. Also, near the contact the quartz diorite has noticeably less quartz and sometimes carries biotite in place of, or with, muscovite.

CHEMICAL ANALYSES

Preparation of samples.—Twelve biotite and seven actinolite samples from adjacent bands of these minerals at the contact between quartz diorite and serpentine-marble have been analyzed in duplicate by rapid analysis methods. The location of these samples, which are all from the southern quarry, is shown in figure 2. Unfortunately, owing to a lack of adequate fresh samples in the field, the sampling is of a somewhat random nature. Ideally several series of samples in each band perpendicular to the contact should be analyzed, since it is likely that a variation in chemical composition of the two minerals occurs perpendicular to the contact.

From each field sample a rough cube, approximately one inch on a side, was cut. The cube was then broken up by mortar and pestle. That part of the sample which passed through a 60-mesh screen, but not through a 140-mesh screen, was kept. Next the sample was purified to 99 percent or better by as many as twenty passes through a Frantz Isodynamic Magnetic Separator. Purity and identity of impurities were checked by sample immersion in refractive index liquids. Minerals other than biotite and actinolite found in one or



more samples were apatite, talc, magnetite, muscovite, tourmaline, and andesine.

All the actinolite samples had the same beta index ($1.630 \pm .003$), as determined in white light. Similarly, all the biotite samples, with the exception of 172, had a beta=gamma index of $1.597 \pm .003$. For 172, beta=gamma = $1.608 \pm .003$. The actinolite was colorless to very light green, and slightly pleochroic from light green to light blue green. The biotite was found to be very light gray green and nonpleochroic, again with the exception of 172, which was light to dark brown and nonpleochroic.

Procedures.—The analytical procedures which were used are based on the work of Shapiro and Brannock (1956). SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , P_2O_5 , and MnO were determined by measuring with a spectrophotometer the transmission of light through sample solutions. An automatic photometric titration technique, using a spectrophotometer and recorder, was used for CaO and MgO . K_2O and Na_2O were measured on a Perkin-Elmer Model 146 flame photometer using lithium as an internal standard. Ferrous iron was found by the conventional titrimetric method. Samples weighing .85 gram were used in a single analysis for the above elements, with .40 gram of this amount used for the ferrous iron determination.

In order to drive off all of the water from minerals such as micas and amphiboles it is necessary to have special equipment, as temperatures of the order of 1200°C must be reached. Such equipment was not available and the water content of the minerals was not determined. This is, of course, unfortunate, because the standard chemical check of addition to 100 percent is eliminated. However, numerous analyses of garnets carried out by these methods did give an excellent 100 percent check (W. C. Phinney, personal communication). A calculation of mineral formulas from the analyses given here is still possible, and the results of such calculations may be found in table 1. The calculations were made by assuming the difference between the total of the chemical work and 100 percent to be all water, and using an atomic basis of 12(O,OH) atoms for biotite and 24(O,OH) atoms for actinolite. The water content of G-1 and W-1 was determined, using the modified Penfield method of Shapiro and Brannock.

The results of the analyses of the three standards and of the biotite and actinolite samples are given in tables 1 and 2. Table 3 shows previously published analyses of seven contact biotite samples and one contact actinolite sample. The biotite and actinolite samples analyzed by Phillips and Hess (1936) were taken at the contact between serpentine and schist at Chester, Vermont, and have also been calculated to an atomic basis to provide a comparison with the work reported here. To provide another comparison, two commercial laboratories analyzed biotite 210. The results reported by these laboratories are included in table 2.

A THERMODYNAMIC TEST OF MINERAL EQUILIBRIUM

If the monomineralic banding has formed strictly as the result of local interaction between two chemically different rock types rather than by introduction of new material by hydrothermal solutions, then necessary conditions

TABLE 1

Chemical analyses and atomic calculations

Sample	Biotite 152		Ave.	Atoms	Biotite 153		Ave.	Atoms
SiO ₂ %	38.74	39.40	39.07	2.758	38.05	38.00	38.03	2.704
TiO ₂ %	.10	.10	.10	.005	.12	.13	.13	.007
Al ₂ O ₃ %	15.89	15.81	15.85	1.318	17.58	18.05	17.81	1.492
Fe ₂ O ₃ %	1.89	1.81	1.85	.098	1.84	1.98	1.91	.102
FeO %	5.64	5.60	5.62	.332	7.78	7.86	7.82	.465
MnO %	.05	.08	.07	.004	.10	.10	.10	.006
MgO %	20.29	20.05	20.17	2.121	18.15	18.03	18.09	1.916
CaO %	1.54	1.60	1.57	.119	.62	.72	.67	.051
Na ₂ O %	.20	.30	.25	.034	.23	.21	.22	.030
K ₂ O %	9.26	8.86	9.06	.815	9.22	9.35	9.29	.842
P ₂ O ₅ %	1.45	1.49	1.47	.088	.69	.67	.68	.041
H ₂ O %	not determined			2.316	not determined			2.489
Total %	95.05	95.10	95.08		94.38	95.10	94.75	

Sample	Biotite 157		Ave.	Atoms	Biotite 158		Ave.	Atoms
SiO ₂ %	39.30	39.28	39.29	2.780	40.31	40.14	40.22	2.846
TiO ₂ %	.04	.02	.03	.002	.16	.14	.15	.008
Al ₂ O ₃ %	18.21	18.39	18.30	1.526	15.69	16.21	15.95	1.330
Fe ₂ O ₃ %	1.99	1.83	1.91	.102	1.57	1.59	1.58	.084
FeO %	5.00	5.04	5.02	.297	5.72	5.62	5.67	.335
MnO %	.02	.04	.03	.002	.02	.05	.04	.002
MgO %	20.75	21.10	20.93	2.206	21.49	20.92	21.20	2.235
CaO %	none	none	none	none	none	none	none	none
Na ₂ O %	.25	.18	.22	.030	.25	.30	.28	.038
K ₂ O %	10.08	9.62	9.85	.888	9.84	10.17	10.01	.904
P ₂ O ₅ %	.11	.09	.10	.006	.14	.10	.12	.007
H ₂ O %	not determined			2.038	not determined			2.255
Total %	95.75	95.59	95.68		95.19	95.24	95.22	

Sample	Biotite 160		Ave.	Atoms	Biotite 167		Ave.	Atoms
SiO ₂ %	42.14	41.97	42.05	2.955	40.14	39.83	39.98	2.836
TiO ₂ %	.02	.06	.04	.002	.76	.74	.75	.040
Al ₂ O ₃ %	14.09	14.44	14.26	1.181	15.82	16.23	16.02	1.345
Fe ₂ O ₃ %	1.59	1.61	1.60	.084	1.96	2.08	2.02	.108
FeO %	4.95	5.05	5.00	.294	5.99	5.98	5.99	.355
MnO %	.06	.05	.06	.004	.02	.07	.04	.002
MgO %	22.69	21.99	22.34	2.338	21.37	21.64	21.51	2.273
CaO %	none	none	none	none	none	none	none	none
Na ₂ O %	.22	.19	.21	.029	.35	.32	.34	.047
K ₂ O %	9.55	9.93	9.74	.874	9.01	8.91	8.96	.810
P ₂ O ₅ %	.03	.07	.05	.003	.04	.03	.04	.002
H ₂ O %	not determined			2.178	not determined			2.057
Total %	95.34	95.36	95.35		95.45	95.83	95.65	

TABLE 1 (Continued)

Sample	Biotite 172		Ave.	Atoms	Biotite 176		Ave.	Atoms
SiO ₂ %	40.42	39.79	40.10	2.871	38.05	37.81	37.93	2.684
TiO ₂ %	1.13	1.14	1.14	.061	.05	.08	.07	.004
Al ₂ O ₃ %	16.67	17.15	16.91	1.427	19.16	19.28	19.22	1.603
Fe ₂ O ₃ %	2.25	2.43	2.34	.126	3.07	3.00	3.04	.162
FeO %	7.96	7.96	7.96	.475	4.02	4.11	4.07	.240
MnO %	.08	.11	.09	.005	.04	.04	.04	.002
MgO %	17.79	18.17	17.98	1.917	21.51	21.78	21.65	2.282
CaO %	none	none	none	none	none	none	none	none
Na ₂ O %	.51	.42	.46	.064	.34	.27	.31	.043
K ₂ O %	9.03	9.00	9.02	.823	9.44	9.33	9.39	.847
P ₂ O ₅ %	.04	.03	.04	.002	.06	.05	.05	.003
H ₂ O %	not determined			1.890	not determined			1.996
Total %	95.88	96.20	96.04		95.74	95.75	95.77	

Sample	Biotite 206		Ave.	Atoms	Biotite 208		Ave.	Atoms
SiO ₂ %	40.14	39.53	39.83	2.818	40.63	40.14	40.39	2.831
TiO ₂ %	.20	.19	.20	.011	.11	.10	.11	.006
Al ₂ O ₃ %	16.61	17.06	16.83	1.403	18.29	18.21	18.25	1.507
Fe ₂ O ₃ %	1.72	1.89	1.80	0.96	1.15	1.11	1.13	.060
FeO %	5.39	5.28	5.34	.316	3.45	3.52	3.49	.204
MnO %	.27	.27	.27	.016	.19	.21	.20	.012
MgO %	20.44	20.57	20.51	2.165	21.15	21.59	21.37	2.231
CaO %	.22	.28	.25	.019	none	none	none	none
Na ₂ O %	.23	.18	.21	.029	.26	.19	.23	.031
K ₂ O %	9.96	9.89	9.92	.895	10.34	10.29	10.31	.922
P ₂ O ₅ %	.37	.34	.36	.022	.13	.11	.12	.007
H ₂ O %	not determined			2.114	not determined			2.056
Total %	95.55	95.48	95.52		95.70	95.47	95.60	

Sample	Biotite 209		Ave.	Atoms	Biotite 210		Ave.	Atoms
SiO ₂ %	40.73	40.14	40.44	2.821	40.56	39.90	40.23	2.827
TiO ₂ %	.12	.11	.12	.006	.05	.04	.05	.003
Al ₂ O ₃ %	16.06	16.01	16.04	1.319	18.65	19.14	18.90	1.565
Fe ₂ O ₃ %	1.49	1.47	1.48	.078	1.29	1.40	1.35	.071
FeO %	2.90	2.89	2.90	.169	3.40	3.33	3.37	.198
MnO %	.06	.06	.06	.004	.08	.09	.09	.005
MgO %	24.27	24.56	24.42	2.538	21.17	21.75	21.46	2.246
CaO %	none	none	none	none	none	none	none	none
Na ₂ O %	.24	.18	.21	.028	.28	.28	.28	.038
K ₂ O %	9.57	9.56	9.56	.850	10.24	10.06	10.15	.909
P ₂ O ₅ %	.11	.08	.10	.006	.09	.08	.09	.005
H ₂ O %	not determined			2.172	not determined			1.888
Total %	95.55	95.06	95.33		95.81	96.07	95.97	

TABLE 1 (Continued)

Sample		Actin. 152		Ave.	Atoms	Actin. 154		Ave.	Atoms
SiO ₂	%	53.77	53.36	53.56	7.571	51.29	51.86	51.33	7.205
TiO ₂	%	.02	.02	.02	.002	.02	.01	.02	.002
Al ₂ O ₃	%	5.78	5.41	5.59	.930	7.90	7.50	7.70	1.275
Fe ₂ O ₃	%	1.78	1.61	1.70	.181	1.68	1.81	1.74	.184
FeO	%	3.76	3.98	3.87	.457	4.01	3.80	3.90	.457
MnO	%	.26	.25	.26	.031	.18	.19	.19	.023
MgO	%	19.72	19.97	19.85	4.180	19.46	19.51	19.49	4.075
CaO	%	12.02	12.34	12.18	1.844	11.69	12.06	11.88	1.786
Na ₂ O	%	.86	.80	.83	.227	1.06	1.08	1.07	.291
K ₂ O	%	.45	.44	.45	.081	.84	.87	.86	.154
P ₂ O ₅	%	.04	.04	.04	.005	.04	.04	.04	.005
H ₂ O	%	not determined			1.555	not determined			1.666
Total	%	98.46	98.22	98.35		98.17	98.23	98.22	

Sample		Actin. 159		Ave.	Atoms	Actin. 161		Ave.	Atoms
SiO ₂	%	56.31	55.96	56.14	7.712	54.02	53.96	53.99	7.173
TiO ₂	%	.01	none	.01	.001	.01	none	.01	.001
Al ₂ O ₃	%	2.07	1.84	1.95	.316	1.35	1.25	1.30	.204
Fe ₂ O ₃	%	.73	.87	.80	.083	.78	.73	.76	.076
FeO	%	2.96	3.02	2.99	.344	2.84	2.88	2.86	.318
MnO	%	.12	.09	.11	.013	.15	.15	.15	.017
MgO	%	21.92	22.13	22.02	4.506	20.59	20.59	20.59	4.075
CaO	%	12.78	12.94	12.86	1.892	13.14	13.54	13.34	1.898
Na ₂ O	%	.45	.39	.42	.112	.31	.25	.28	.072
K ₂ O	%	.23	.27	.25	.044	.24	.20	.22	.037
P ₂ O ₅	%	trace	.02	.01	.001	none	none	none	none
H ₂ O	%	not determined			2.235	not determined			5.758
Total	%	97.58	97.53	97.56		93.43	93.55	93.50	

Sample		Actin. 166		Ave.	Atoms	Actin. 171		Ave.	Atoms
SiO ₂	%	57.09	56.52	56.80	7.802	56.57	56.07	56.32	7.755
TiO ₂	%	.02	.01	.02	.002	.01	none	.01	.001
Al ₂ O ₃	%	1.35	1.27	1.31	.212	1.82	1.75	1.78	.288
Fe ₂ O ₃	%	.95	.82	.89	.092	.92	1.04	.98	.101
FeO	%	3.42	3.55	3.48	.399	3.82	3.78	3.80	.437
MnO	%	.17	.14	.16	.019	.18	.16	.17	.020
MgO	%	22.04	21.90	21.97	4.495	21.77	21.93	21.85	4.482
CaO	%	12.03	12.42	12.22	1.798	11.78	11.98	11.88	1.752
Na ₂ O	%	.36	.36	.36	.096	.44	.43	.44	.117
K ₂ O	%	.18	.22	.20	.035	.23	.26	.25	.044
P ₂ O ₅	%	.11	.09	.10	.012	.02	trace	.01	.001
H ₂ O	%	not determined			2.280	not determined			2.304
Total	%	97.72	97.30	97.51		97.56	97.40	97.49	

TABLE 1 (Continued)

Sample		Actin. 175		Ave.	Atoms	Actin.	Atoms	Biot.	Atoms
								(Phillips and Hess, 1936)	
SiO ₂	%	58.66	58.03	58.34	7.829	53.27	7.619	38.72	2.843
TiO ₂	%	.01	none	.01	.001	.06	.006	.47	.026
Al ₂ O ₃	%	.03	none	.02	.003	4.92	.829	18.39	1.591
Fe ₂ O ₃	%	.59	.53	.56	.057	1.43	.154	1.05	.058
FeO	%	2.23	2.34	2.28	.256	6.78	.811	9.54	.585
MnO	%	.12	.08	.10	.011	.20	.024	.16	.010
MgO	%	24.73	25.06	24.90	4.977	19.47	4.148	18.44	2.017
CaO	%	9.85	10.22	10.04	1.443	11.70	1.792	trace	trace
Na ₂ O	%	.19	.19	.19	.049	.75	.208	.68	.097
K ₂ O	%	.06	.09	.08	.014	.59	.108	9.74	.912
P ₂ O ₅	%	trace	none	trace	trace	.11	.013	.11	.007
H ₂ O	%	not determined			3.114	.44	.687	.69	1.322
Total	%	96.47	96.54	96.52		99.72		97.99	

Sample	Calculated Atomic Formula	Sample	Calculated Atomic Formula
Bio. 152	A _{1.97} B _{2.73} C _{4.00} O _{9.08} (OH) _{2.88}	Act. 152	A _{2.15} B _{5.80} C _{8.00} O _{22.44} (OH) _{1.08}
Bio. 153	A _{1.00} B _{2.78} C _{4.00} O _{9.01} (OH) _{2.40}	Act. 154	A _{2.28} B _{5.80} C _{8.00} O _{22.33} (OH) _{1.67}
Bio. 157	A _{1.00} B _{2.82} C _{4.00} O _{9.04} (OH) _{2.04}	Act. 159	A _{2.08} B _{4.80} C _{8.00} O _{21.78} (OH) _{2.26}
Bio. 158	A _{1.04} B _{2.85} C _{4.00} O _{9.74} (OH) _{2.26}	Act. 161	A _{2.01} B _{4.40} C _{7.88} O _{21.24} (OH) _{5.78}
Bio. 160	A _{1.00} B _{2.80} C _{4.00} O _{9.03} (OH) _{2.18}	Act. 166	A _{1.88} B _{5.00} C _{8.00} O _{21.72} (OH) _{2.98}
Bio. 167	A _{1.06} B _{2.86} C _{4.00} O _{9.04} (OH) _{2.04}	Act. 171	A _{1.01} B _{5.00} C _{8.00} O _{21.70} (OH) _{2.20}
Bio. 172	A _{1.00} B _{2.80} C _{4.00} O _{10.11} (OH) _{1.80}	Act. 175	A _{1.01} B _{5.80} C _{7.88} O _{20.80} (OH) _{2.11}
Bio. 176	A _{1.00} B _{2.85} C _{4.00} O _{10.00} (OH) _{2.00}	Act.	A _{2.11} B _{5.80} C _{8.00} O _{22.21} (OH) _{1.00}
Bio. 206	A _{1.08} B _{2.80} C _{4.00} O _{9.00} (OH) _{2.11}	(Phillips and Hess, 1936)	
Bio. 208	A _{1.00} B _{2.80} C _{4.00} O _{9.04} (OH) _{2.00}	A = (K, Na, Ca)	
Bio. 209	A _{1.00} B _{2.94} C _{4.00} O _{9.00} (OH) _{2.17}	B = (Mg, Fe'', Fe''', Ti, Mn, Al)	
Bio. 210	A _{1.00} B _{2.82} C _{4.00} O _{10.11} (OH) _{1.80}	C = (Si, Al, P)	
Bio.	A _{1.01} B _{2.14} C _{4.00} O _{10.00} (OH) _{1.88}		

of the equilibrium state to which this process would tend can be outlined. Although the possible attainment of these conditions cannot be tested with respect to temperature and pressure, it can be partially tested with respect to composition. This has been the purpose of the chemical analyses. This section is included to indicate briefly the theoretical basis for the experimental work.

We will define our system of interest to be made up of a small length (a few feet, for example) of the two monomineralic bands. The system would be centered at the contact between the two bands and would include all material on either side of the contact which had been altered by interaction across the contact. The necessary conditions that must exist for equilibrium during the formation of the minerals are (1) that the temperature of all phases (minerals) be equal, (2) that the pressure on all phases be equal, and, (3) that the chemical potential of each component be the same in all phases in which it is present.

By dealing with a small system the equal pressure requirement can be assumed to have existed. A temperature gradient perpendicular to the contact may have existed at the time of formation of the banding. If it did, the composition of the minerals might reflect this by exhibiting a compositional gradient perpendicular to the contact. We will assume that both the temperature and pressure requirements have been satisfied.

Let us consider the biotite grains in the biotite band. These are different examples of the same phase, namely: $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$. In particular we are interested in the Mg/Fe ratio of the different grains. If we assume that the magnesium and iron ions in a biotite grain represent an ideal mixture, i.e., that either ion can substitute equally well in the structure, then the chemical potentials of magnesium and iron in the grain can be expressed as:

$$\mu_{Fe}^a = \mu_{Fe}^0 + RT \log \bar{n}_{Fe}^a$$

and:

$$\mu_{Mg}^a = \mu_{Mg}^0 + RT \log \bar{n}_{Mg}^a$$

where μ_{Fe}^0 refers to the chemical potential of iron in the pure state, μ_{Mg}^0 to the chemical potential of magnesium in the pure state, and $\bar{n}_{Fe}^a$ refers to the mole fraction of iron based on the total number of moles found in six-fold coordination, $\bar{n}_{Mg}^a$ to the mole fraction of magnesium on the same basis.

The assumption of ideal behavior is necessary to avoid use of activity coefficients, which give a quantitative measure of the discrepancies between actual behavior of a mixture and so-called "ideal" behavior. Ideal behavior is defined by certain thermodynamic relationships and represents the simplest possible behavior. We have very little information on the degree of ideality of mineral solid solutions, and no numerical values for the pertinent activity coefficients. The assumption of an ideal mixture for the magnesium and iron ions in biotites is thus an approximation. The two ionic radii do not differ greatly in size, a necessary condition for ideal behavior.

Assuming equilibrium has been attained in the biotite band, the necessary conditions of this state require that for two biotite grains α and β :

$$\mu_{Fe}^a = \mu_{Fe}^b \text{ and } \mu_{Mg}^a = \mu_{Mg}^b$$

Therefore: $\bar{n}_{Fe}^a = \bar{n}_{Fe}^b$ and $\bar{n}_{Mg}^a = \bar{n}_{Mg}^b$.

Thus, if we could analyze two separate biotite grains which have been formed in equilibrium with each other, the mole fraction of iron in each grain should be the same, as should be the mole fraction of magnesium. Naturally, in actual chemical analysis, a number of grains from one sample must be compared with a number of grains from another sample.

However other elements, such as aluminum, may substitute for iron and magnesium, and these other elements may not behave ideally with respect to each other. In this case, even though

$$\mu_{Fe}^a = \mu_{Fe}^b \text{ and } \mu_{Mg}^a = \mu_{Mg}^b, \bar{n}_{Fe}^a \neq \bar{n}_{Fe}^b \text{ and } \bar{n}_{Mg}^a \neq \bar{n}_{Mg}^b$$

For this situation the mole fractions of iron and magnesium should be based on the total number of moles of iron and magnesium only. Using this basis equilibrium requires:

$$\frac{\bar{n}_{Fe}^a}{\bar{n}_{Mg}^a + \bar{n}_{Fe}^a} = \frac{\bar{n}_{Fe}^b}{\bar{n}_{Mg}^b + \bar{n}_{Fe}^b} \text{ and } \frac{\bar{n}_{Mg}^a}{\bar{n}_{Mg}^a + \bar{n}_{Fe}^a} = \frac{\bar{n}_{Mg}^b}{\bar{n}_{Mg}^b + \bar{n}_{Fe}^b}$$

Thus attainment of equilibrium can still be checked by measuring and com-

paring a ratio such as $Mg/(Mg + Fe)$ in biotite grains. In actual calculations a basis of 12 (O, OH) atoms can be used to compute the number of magnesium and iron atoms represented by a given analysis, with the desired ratio then derived from these numbers.

Similar reasoning could be used to test attainment of equilibrium in a large homogenous mass of rock, provided the constant temperature and constant pressure requirements can be assumed to have been fulfilled. Thus the $Mg/(Mg + Fe)$ ratio would be a constant in biotite grains scattered through a pelitic schist which had formed under equilibrium conditions. A systematic change in the ratio in a particular direction might indicate a temperature gradient or metasomatic movement of material. It is essential in studying metasomatism to check a rock for variations in mineral chemical composition rather than for variations in its bulk composition.

In a recent publication Kretz (1959) presents 62 spectrochemical analyses of coexisting biotite, garnet, and hornblende from Grenville gneisses of Quebec and discusses the results in terms of phase equilibrium. In testing the attainment of thermodynamic equilibrium in these rocks he emphasizes use of the distribution coefficient for a given element between different minerals. It is concluded that a close approach to equilibrium was reached.

DISCUSSION OF RESULTS

Precision and accuracy.—A discussion of advantages and results obtainable in rapid analysis of silicate rocks is given by Shapiro and Brannock (1956). Mercey (1956) presents a detailed study of the accuracy and precision of the rapid methods as applied to rock analysis. He concludes that the accuracy and precision of these methods compare favorably with results obtainable by conventional methods. The author concurs in this conclusion, provided duplicate samples are analyzed and each sample is run in duplicate. The latter qualification adds relatively little to the total time required for the rapid techniques and is a necessity since aberrant results do occur frequently enough to be significant. The concurrence applies only to analyses of samples with element concentration ranges of common igneous rocks. A further qualification must be made for the application of these methods to mineral analysis. In this case unusually high or low concentrations of various elements occur, and results comparable to those of conventional methods may not be obtainable.

The calculated atom values given here show good agreement between the chemical analyses and the requirements of the crystal chemistry of mica and amphiboles. For example, the sum of the cations of an amphibole should fall between fifteen and sixteen, and this value varies from 14.96 to 15.51 for five of the analyzed actinolites. The total for 175 is 14.64 and for 161, 13.88. The low summation of the chemical analysis of 161 indicates the probable presence of another major constituent. The analyses of the three standards provided another check on the mineral analyses, with results for the standards being similar to those obtained by conventional methods. The analyses of biotite 210 by the two commercial laboratories show wide disagreement in the results for several elements, and neither laboratory shows close agreement with the

TABLE 3
Published analyses of contact biotite and actinolite samples

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O	Total
Biotite Also reported: Fluorine—.76 (Emerson, 1886, Chester, Mass.; Contact of plagioclase vein in talc-chlorite seam)	39.08		15.38	7.12	.31	23.58		2.63	7.50		2.24	98.60
Biotite (Emerson, 1886, Chester, Mass.; Contact of plagioclase vein in talc-chlorite seam)	39.55		15.95	7.80		22.25		(10.35)			4.10	100.00
Biotite Also reported: Fluorine—2.89 (von Eckermann, 1925, Mansjo, Sweden; Pegmatite-limestone contact)	40.80	.05	13.16	1.84	2.16	26.72	.46	2.44	7.95		2.95	101.42
Biotite Also reported: Fluorine—1.67; Cr ₂ O ₃ —.02 (Barth, 1936, Dutchess County, N. Y.; Pegmatite-schist contact)	37.39	2.48	20.17	2.08	14.32	9.80	.51	.87	8.56		3.03	100.88
Biotite Also reported: Fluorine—present but not determined (Phillips and Hess, 1936, Chester, Vermont; Serpentine-schist contact)	38.72	.47	18.39	1.05	9.54	18.44	trace	.68	9.74	.11	.69	97.99
Biotite Also reported: Fluorine—4.34; Li ₂ O—.120; Rb ₂ O—.185; Cs ₂ O—.47 (Hess and Stevens, 1937, Kings Mt., North Carolina; Mica schist-pegmatite contact)	42.02	1.35	18.75	.66	8.29	9.55	.93	.73	8.54		2.60	101.55
Biotite Also reported: Fluorine—3.17; Li ₂ O—.65; Rb ₂ O—.148; Cs ₂ O—1.12 (Hess and Stevens, 1937, Tin Mt., South Dakota; Mica schist-pegmatite contact)	39.97	2.64	17.51	2.26	14.81	8.45	none	.45	8.48		2.80	104.01
Actinolite (Phillips and Hess, 1936, Chester, Vermont; Serpentine-schist contact)	53.27	.06	4.92	1.43	6.78	19.47	11.70	.75	.59	.11	.44	99.72

author's values. This points out the importance of evaluating a mineral analysis by a crystal chemistry check.

General results.—Not unexpectedly, a rather large variation occurs in the composition of the two minerals. The major element variations in the biotites are SiO_2 : 37.93—42.05%; Al_2O_3 : 14.26—19.22%; FeO : 2.90—7.96%; Fe_2O_3 : 1.13—3.04%; MgO : 17.98—24.42%; and K_2O : 8.96—10.31%. In the actinolites the variations are SiO_2 : 51.33—58.34%; Al_2O_3 : .02—7.70%; FeO : 2.28—3.90%; Fe_2O_3 : .56—1.74%; MgO : 19.49—24.90%; and CaO : 10.04—13.34%. These variations, most of which are too great to be attributed to experimental error, indicate that only one or two analyzed specimens are an inadequate sample of the composition of such contact minerals.

Biotite samples 167 and 172 were taken where pelitic schist replaces quartz diorite as wall rock of the bands. The only difference in chemical composition of these samples is their high content of TiO_2 as compared to that of the other biotites. In the case of 172, which has 1.14% TiO_2 , the color and

TABLE 4

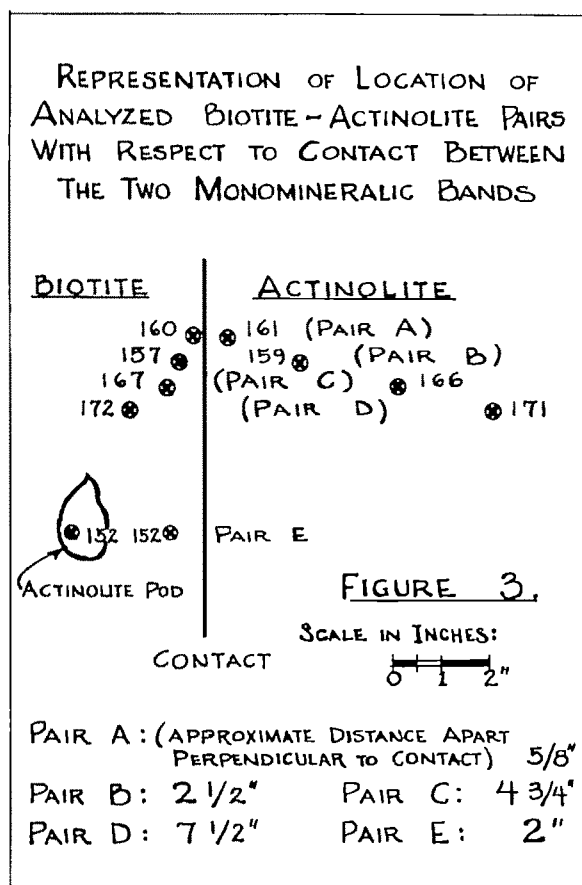
Calculated $\text{Mg}/(\text{Mg} + \text{Fe})$ atomic ratios in biotite and actinolite samples

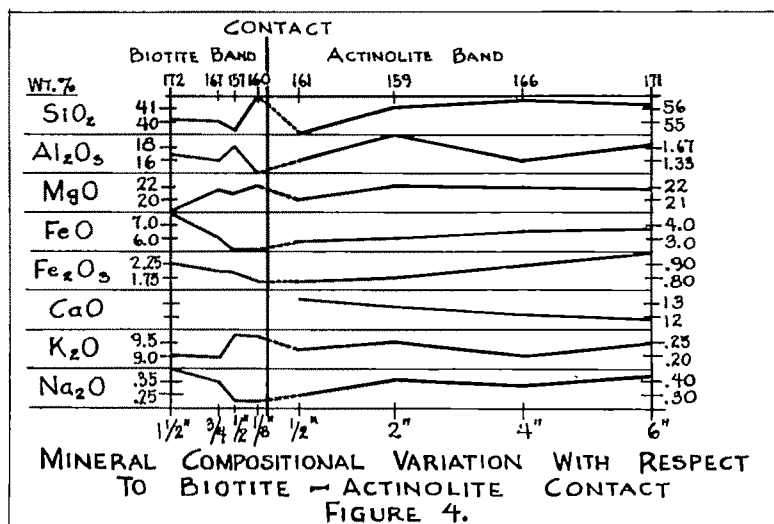
Biotite	Atoms Mg	Atoms Fe	Mg/(Mg + Fe)
152	2.121	.332	.865
153	1.916	.465	.805
157	2.206	.297	.881
158	2.235	.335	.870
160	2.338	.294	.888
167	2.273	.355	.865
172	1.917	.475	.801
176	2.282	.240	.905
206	2.165	.316	.878
208	2.231	.204	.916
209	2.538	.169	.938
210	2.246	.198	.919
Actinolite	Atoms Mg	Atoms Fe	Mg/(Mg + Fe)
152	4.180	.457	.901
154	4.075	.457	.899
159	4.506	.344	.929
161	4.075	.318	.928
166	4.495	.399	.918
171	4.482	.437	.911
175	4.977	.256	.951

index of the mineral differ from those of the other biotites, apparently because of the titania content. No change in titania content is shown by the coexisting actinolite samples of these two biotites.

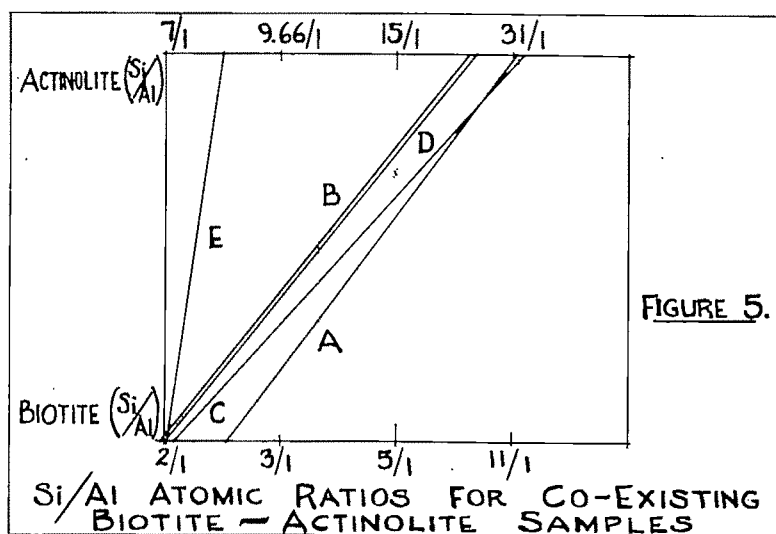
High contents of CaO and P_2O_5 in biotite samples 152 and 153 would seem to indicate appreciable apatite impurity. However, the samples were carefully checked by immersion in refractive index liquids and no apatite was found.

The variation in the $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios in the two minerals indicates a degree of chemical disequilibrium in the bands, since it has been shown that attainment of equilibrium requires that the $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios in different samples of the same mineral be similar (see table 4). However, no pair of samples of the same mineral were taken closer together than one foot. Biotite samples 157 and 158 occurred one foot apart and have ratios of .881 and .870 respectively. This may indicate that local equilibrium between grains adjacent to each other or a few inches apart was reached.





Biotite-actinolite pairs.—A schematic representation of the relation of the analyzed biotite-actinolite pairs to the contact between the two monomineralic bands is shown in figure 3. Figure 4 shows the variation in composition with respect to the contact between the two bands. As already pointed out, the four mineral pairs of figure 4 do not actually come from one line across the two bands. Each pair is from a different point along the contact, with one pair from another contact, as has been shown in figure 2. It is likely that figure 4 represents the kind of variation which exists perpendicular to the contact. This is seen as culminations and depressions in the element content of the two minerals in the vicinity of the contact. A similar result was found by Dennen



(1951) at the contact between certain intrusives and their wall rock. He reported: "highly irregular variations are found when the intrusive and wall rock were compositionally different and steep thermal gradients existed. These latter variations may show geochemical culminations and depressions that are wave-like in form and die out in both directions from the contact zone." This work indicates that the variations found by Dennen in contact rocks exist also in contact minerals.

Figures 5 and 6 show the relationship of the Si/Al and Mg/Fe atomic ratios of the coexisting biotite-actinolite pairs. It is interesting to note that pair E, which was taken at the contact of an actinolite pod in the biotite band, and therefore represents a definite disequilibrium situation, has a much different slope in both diagrams as compared to the other pairs, which were taken across the main contact between the two bands. Assuming that Mg and Fe have been introduced from the serpentine-marble, and Si and Al from the quartz diorite-schist, the change in slope of the pairs away from the main contact indicates silica to be more mobile than aluminum, and iron to be more mobile than magnesium.

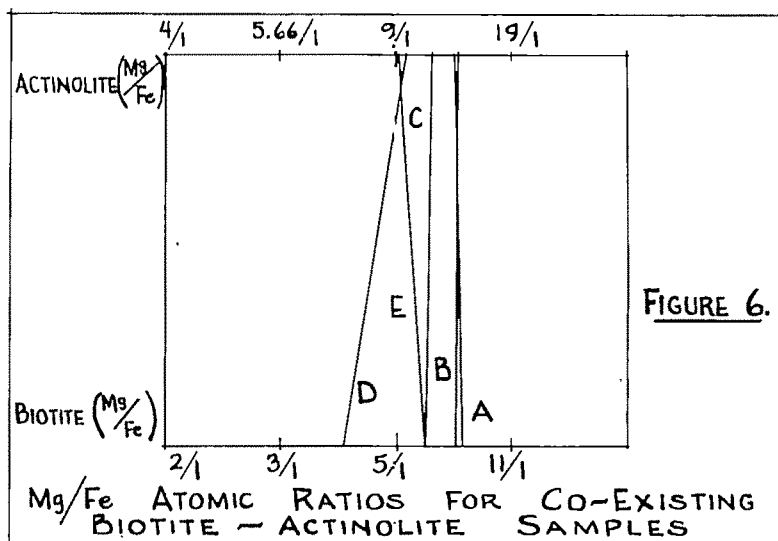


FIGURE 6.

CONCLUSIONS

The monomineralic bands appear to be the result of very local reaction at the contact of the intrusive quartz diorite with the serpentine-marble. The chemical results show a large variation in the composition of the minerals. This fact, and the variation in the $Mg/(Mg + Fe)$ ratios of the two minerals, indicates that general thermodynamic equilibrium had not been reached at the time of formation of the bands. This is not an unexpected result, since minerals in such contact areas would be formed rapidly, without time for adjustments in distribution of elements, such as might occur in a slowly cooling magma or in regional metamorphism.

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MICROSTRIATIONS ON POLISHED PEBBLES

SHELDON JUDSON* and RONALD E. BARKS**

ABSTRACT. Very small striations, here called *microstriations*, occur on the smooth, polished surfaces of some pebbles. They average a millimeter or less long and are commonly less than 0.05 mm wide.

Microstriations of random direction occur on artificially polished pebbles, and also on pebbles from beach and fluvial environments. Microstriations parallel to one another and oriented in sets occur on pebbles from various stratigraphic units including the Cloverly, Morrison, Wapiabi, and Windrow formations. These particular oriented microstriations are thought to be due to tectonic movement or compaction or both.

INTRODUCTION

Surface textures of pebbles are sometimes useful in the reconstruction of geologic history. Examples include the surfaces of glaciated pebbles and ventifacts as well as the shiny surfaces of stones coated with desert varnish. This paper reports on an additional characteristic of pebble surfaces that reflects geologic history, namely striations of very small size, here called *microstriations*.

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MICROSTRIATIONS

Description

Microstriations occur either as preferentially oriented scratches in one or more sets on a pebble surface or as random scratches. Their length ranges up to over 2 mm but averages between 0.25 and 1 mm. In width they are less than 0.1 mm and usually less than 0.05 mm. One can see the larger ones without magnification. In most instances, however, a hand lens or binocular microscope is needed to detect them, and in all cases some magnification enables easy observation. Most microstriations are sharp, well-defined continuous grooves. Some, however, are discontinuous, and a few consist of a series of linear chip-marks on the pebble surface.

Microstriations occur on smooth, usually polished surfaces. The higher the polish the more finely inscribed are the microstriations. Polished surfaces are usually confined to siliceous or fine-grained material. We have observed microstriations on pebbles from deposits ranging in age from Jurassic to the present. They are found on pebbles which have been both artificially or

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naturally shaped and polished. They are not restricted to a single environment or history.

Artificially produced microstriations.—Pebbles rounded and polished in tumbling machines for the jewelry trade carry microstriations. They are visible only with magnification. They are straight, narrow, and of uniform width throughout. They are randomly oriented and can occur any place on the pebble (pl. 1-A). Examination of a sample of 36 commercially polished pebbles showed that the microstriations were common on 12 and present but rare on the remaining 24. The sample included pebbles of quartz, chert and agate as well as a single pebble of granite.¹

The general technique of shaping and polishing the pebbles is fairly standard, although each producer tends to introduce variations into the method. The basic procedure is given in Sheridan (1958, p. 56). All stages of the process are carried out in revolving drums or barrels, whose capacities range from eight or ten pounds of stones up to two or three tons. Water is essential in all stages, and progressively finer abrasives are used in each stage.

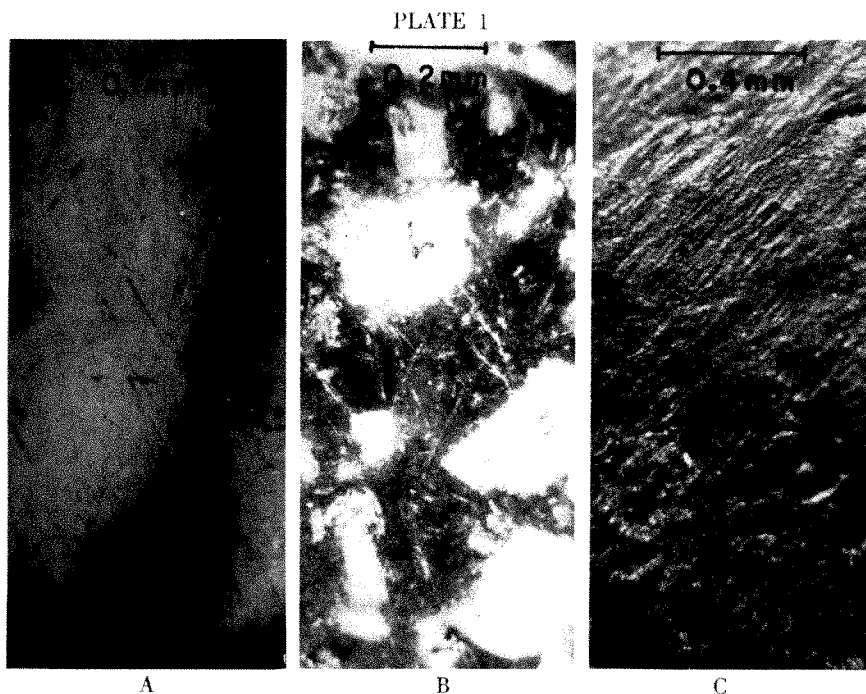
The scratches on the final polished surface seem to be acquired during the polishing stage. An examination of approximately 50 pebbles of clear quartz processed through the second stage of tumbling showed no striations. After the polishing or final stage of tumbling, minute, randomly oriented striations were present on the three pebbles of clear quartz available for examination.

Microstriations on modern beach pebbles.—Polished pebbles occur on several beaches along the California coast south of San Francisco, particularly at Pebble Beach just north of Pescadero Point, and at Lobos State Park south of Carmel. Some of these pebbles exhibit microstriations, and these occur randomly as shown in plate 1-B. These striations are not as clearly inscribed as those on artificially polished pebbles, probably because the natural polish is not as well developed as the artificial polish. In addition to the microstriations, crescent-shaped scars of percussion or impact also occur. These are more common than the straight scratches, which we assign to abrasion as the pebble itself is moved either in the surf zone, or in the quieter swash zone of the beach, or in both.

Microstriations on stream gravels.—An examination of cassiterite pebbles from the placer deposits of Cornwall, England (Princeton University Mineralogical Collection, #5-248) has revealed a few randomly occurring microstriations. Similar striations are present on the semipolished surface of a pebble of magnetite taken from a creek bed at Gabb's, Newfoundland (Princeton University Mineralogical Collection, #79-237).

Small striations, but visible to the unaided eye and measuring up to 0.3 mm in width, occur on well-rounded but mat-surfaced, disk-shaped pebbles of Devonian red, sandy shale collected from the high water channel of Brodhead Creek, about two miles upstream from Stroudsburg, Pennsylvania. The striations are arranged in two or more sets, and within the sets the individual striations are parallel. The striations are generally broader at their centers

¹ The pebbles were supplied from stock by the International Gem Corporation, 15 Maiden Lane, New York City.



A. Microstriations on surface of a pebble artificially polished in tumbling machine.

B. Microstriations on surface of a pebble from Pebble Beach near Pescadero Point, California.

C. Microstriations on surface of a pebble from the Wapiabi formation of Cretaceous age, Alberta, Canada.

than at their ends. The pebbles were found embedded in a sandy matrix with only their upper surface exposed. These pebbles are part of a recent fluvialite deposit and were probably exposed during the catastrophic flood of September 1955. Similar striations were found on pebbles just below Buck Hills falls, Pennsylvania, near the headwaters of Brodhead Creek. These pebbles lay in gravels moved during the same flood. We do not think that the striations are glacial, not only because the pebbles come from a stream deposit but also because the striations differ in their intensity and arrangement from those that can be definitely assigned to glacier action.

Similar but still larger striations are present on quartzite pebbles collected from deposits reflecting torrential stream conditions along Naked Creek four miles north of Elkton, Virginia on the eastern side of the Shenandoah Valley.

Microstriations on pebbles from the Wapiabi formation.—Pebbles from the Muskiki member of the folded and faulted Wapiabi formation of Cretaceous age in the Alberta foothills exhibit areas of well-oriented microstriations. The pebbles, collected by D. F. Stott, are considered by him (1958, p. 165) to represent the shoreline deposits of an advancing sea. The pebbles range in size from 5 to 75 mm in maximum dimensions, are well rounded, and many

are disk-shaped. A dark gray chert is the dominant lithologic material but some quartzite and sandstone pebbles also occur. A few of the pebbles are pressure-pitted. A black, "varnish"-like veneer occurs in patches and has a very high luster. It chips or flakes off the pebbles and appears similar to desert varnish. It is on these patches of varnish and on areas immediately adjacent to them that we have found the microstriations.

The striations parallel each other and are generally less than 0.05 mm in width and less than 1 mm in length (pl. 1-C). They are straight and shallow and many taper toward their ends. In some instances, where the striations are abundant, they fall into a general pattern across the greater part of the pebble. Plate 2-A shows a concentric pattern of the striations on one such pebble.

Crescent-shaped scars of percussion are also present on the Wapiabi pebbles. In some places the finer parallel striations partly obscure the impact crescents, and in other places the percussion scars lie beneath the "varnish" veneer of the pebbles. These percussion scars, then, antedate both the "varnish" and the oriented striations.

Microstriations on so-called "gastroliths".—We have observed microstriations on 81 out of 91 pebbles collected from the Cloverly and Morrison formations. The pebbles are predominantly chert and quartz and are red, yellow, black, or white. Their maximum dimension ranges from 5 to 75 mm. Each pebble is polished and might on this basis be called a "gastrolith".

The microstriations are both random and oriented. The random striations were found on 81 pebbles. Of these 32 also showed oriented striations. Where a sequence can be determined, the oriented striations postdate the random scratches as well as crescent-shaped impact scars which are present on most pebbles.

The oriented scratches may take different patterns and forms. Thus the nonrandom microstriations may be oriented not only in respect to one another but also to the entire pebble, as shown in plate 2-B. In other pebbles two or more sets or patches of striations occur. Individual striations parallel each other within any given set but diverge from the direction of striations in neighboring patches.

The details of individual microstriations differ. Plate 3-A shows the most commonly seen types in which the microstriations are close, straight, sometimes deeper and wider at their centers, and sometimes of constant width throughout. Some microstriations are curved and some are short, with curved gouges deeper at one end as shown in plate 3-B. The oriented microstriations postdate the random, somewhat larger scratches.

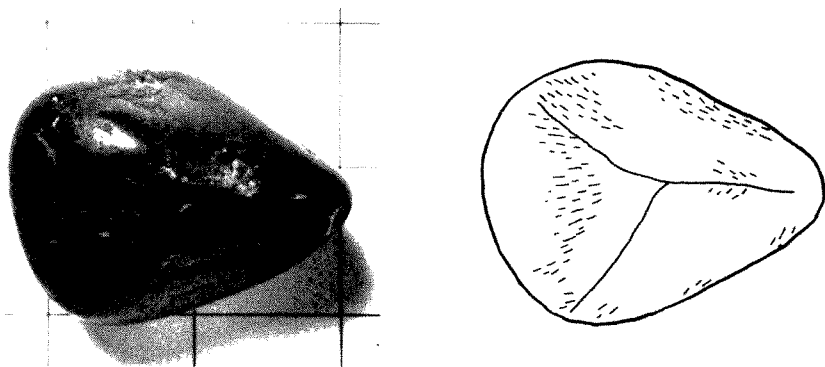
The striations are most common and best developed along the areas immediately adjoining the ridges that separate adjacent faces of the pebble.

The polished pebbles of the Windrow formation of Cretaceous (?) age have been referred to as gastroliths (Stauffer, 1945). A few microstriations were observed on small pebbles of quartz and chert collected from exposures of the Windrow formation near Tomah, Wisconsin. The pebbles are small, up to 10 mm in maximum size. The striations are both random and parallel. They are rare on the pebbles examined, and the parallel striations are very small.

PLATE 2



A. Orientation of microstriations on a pebble from the Wapiabi formation. Squares 25 mm (about 1 inch) on the side.



B. Orientation of microstriations on a pebble from the Cloverly formation, Wyoming. Scale as in A.

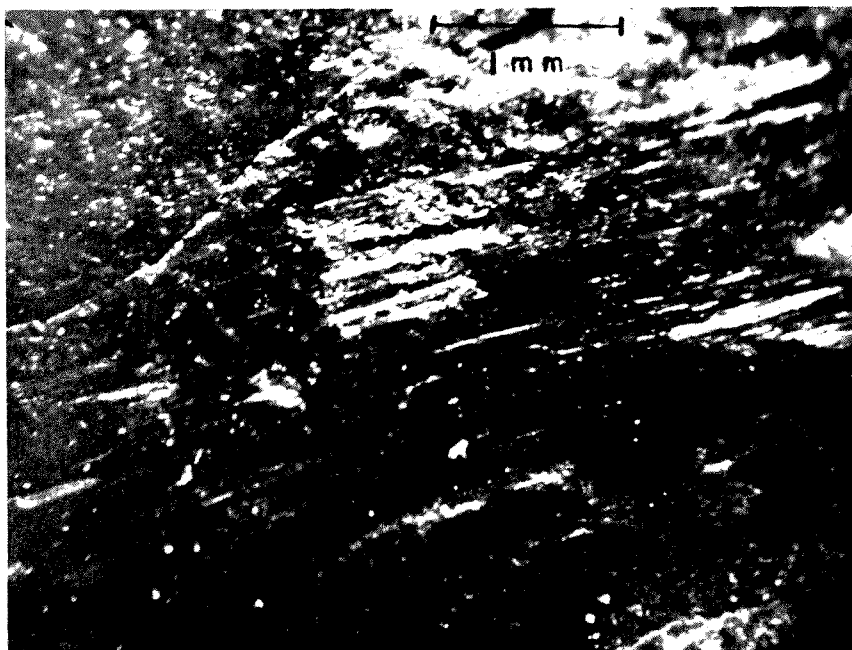
Origin

Bryan (1931) makes casual reference to "minute" parallel grooving observed on polished pebbles from the Morrison formation. We have found no other mention to features we call microstriations. Striations of megascopic size, however, are attributed to a wide variety of causes, and microstriations logically may be expected to result from one or more of these causes. What processes, then, produce striations?

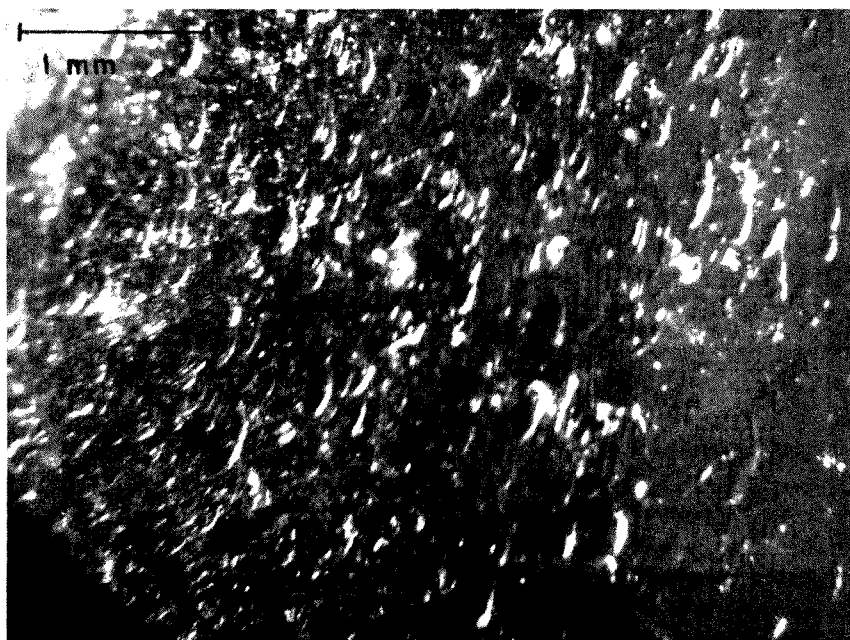
Louis Agassiz' statement of the glacial theory in 1840 included a discussion of glacially striated rock. Since then a few studies of glacial striations (Chamberlin, 1888; von Engeln, 1930) have appeared. Unless proved otherwise, striations on bedrock and boulders have generally been assigned to glacial action.

Penck (1884) and Hughes (1895, p. 101) point out that pebbles may be striated by tectonic processes and that such striations may be mistaken for evidence of glacial action. Hughes (1898, p. 115) says that the scratches on a tectonically striated pebble "often appear pinched out and scored on both sides up to the edge" and that the "grooves follow the curvature of the stone". Subsequently several writers, including Freitag and Kästner (1909), Woodworth (1912), Götzinger (1914), Gregory (1915), Deeke (1920), Dunbar (1924), Voitești (1925), and Krecji-Graf (1927), have referred to tectonically striated

PLATE 3



A. Straight parallel microstriations on surface of pebble from the Cloverly formation.



B. Crescent-shaped gauges on surface of pebble from the Cloverly formation.

stones. In 1906 McCollie observed that pebbles from a stretched pebble conglomerate showed striations parallel to their long axes. More recently Pettijohn (1956, p. 71) writes that "pebbles or cobbles in a rather fine-grained matrix may be striated or slickensided as a result of internal movement during deformation of the rock under pressure".

Hayden (1911, p. 40) reports pebbles with glacial-like striations from northern Afghanistan. These pebbles also bear the marks of wind pitting, and for this reason Hayden assigns the striations to wind action, a conclusion that appears otherwise unsupported. On the other hand Hovey (1909, p. 413) cites evidence that sand blast during the Mont Pelée eruptions in 1902-1903 produced striations on bed rock "similar to glacial" striations. They were 2 to 10 cm deep and 10 to 15 meters long. Hovey makes no reference to striations on individual pebbles or to small scale striations, but Cailleux (1942, p. 49) and Sharp (1949) describe fine fluting and grooving on ventifacts. Bryan (1931) suggests that the minute grooving on Morrison pebbles may be due to wind-driven material.

Mass movement of material has long been known as an effective process of striating rock. Penck (1883, p. 172; 1884) reports blocks striated by landslide movement. Wright (1892, p. 477) points to landsliding as a process producing pseudo-glaciated boulders and notes that small, artificially induced slides on slopes of slate spoil produce striations on some fragments. Meunier (1894) describes striations due to mass movement under experimental conditions. Hughes (1898, p. 116) records striations due to landslips, and Hovey (1909, p. 412) describes striations associated with avalanching during the Peléean eruptions. Breuil (1934, p. 270; pl. XXIV) reports and illustrates striations on pebbles and cobbles from the solifluction deposits of the Somme Valley, France. Similar striations are reported by Heim (1936, p. 452) from eastern Tibet and by Büdel (1936, p. 19) from unglaciated central Europe.

Krecji-Graf (1927) cites the mudflow as an agent that striates boulders, as do Pack (1923, p. 353), Scrivenor (1929), Blackwelder (1930), Sharpe (1938, p. 59), Sharp and Nobles (1953, p. 558) and Thornbury (1954, p. 92). Van Houten (1957) demonstrates that the Gunnison and Ridgeway conglomerates of Colorado, which carry abundant striated pebbles and cobbles, are most probably mudflow deposits rather than glacial deposits as originally interpreted by Atwood (1915).

Dyson (1937, 1938) and Imamura (1937, 1938) have simultaneously but independently reported on the effectiveness of snowslide avalanches as a process of striation.

Feilden and De Rance (1878) observed that sea ice driven ashore by high winds striates or "glaciates" stones. Dawson (1894, p. 105-110) repeats this observation and comments that the striation is confined to the exposed portion of the beach pebbles. Leffingwell (1919, p. 174) found a few stones on the Alaskan coastal plain that suggested striation by wind-driven sea ice, but he did not believe such stones could be mistaken for those transported by a glacier. Washburn (1947, p. 47), working on Victoria Island, found that not only did sea ice striate beach stones but that except for lack of faceting, such stones were difficult to distinguish from a stone carried by glacier ice.

Russell (1890, p. 117-120) reports that river ice of Alaskan rivers striate, facet, and polish stream gravels. The pebbles, embedded in clay matrix, are abraded by river ice, which scrapes across their exposed upper surface. Striations are generally parallel to the river flow, and the affected pebbles are similar to a pebble from a glacier except that the scratches are "less regular and less firmly drawn than the grooves and striations on typical glaciated pebbles". Wentworth (1928) invoked river ice to account for striated stream gravels found in terrace deposits along the rivers of the southern states. He found the striations on smooth-surfaced siliceous stones. He reports them to be clearly cut and uniform in width throughout. Their width ranges from 0.3 mm to 1 or 2 mm and their length 5 to 10 cm. They are most abundant on flat surfaces and over the edges from the flat areas. Some of the striations occur in strongly marked systems oriented in the same direction. More commonly two or three well-defined systems cross each other and are mingled with a few short, sometimes curved striations with no systematic arrangement. Later Wentworth (1932) studied the work of ice jams in arctic rivers and records striations similar to those found in the southern rivers, but gives no detailed description.

Du Pasquier (1897) invoked torrential stream flow without the intervention of ice to account for striations on blocks and cobbles in stream channels. Lugeon (1913) describes striated and polished bedrock in the Yadkin River, North Carolina, and (1921) in the Ardèche River of France. He postulates that the striations are cut by sand driven in jetlike flow and that the polishing is the result of a heavy silt load in the river.

The literature refers almost exclusively to large striations easily visible to the naked eye. On the other hand, the processes which produce these large striations could very conceivably produce the microstriations we have described. In considering the cause of microstriations it is apparent that we are dealing with two general types of microstriations, namely (1) single microstriations occurring randomly and (2) microstriations parallel to one another and arranged in one or more systems.

Microstriations of random occurrence.—Random striations demand that either the striating agent, or the pebble being scratched, or both, are free to move in many different directions. This situation occurs in the tumbling machine, and we have found that random microstriations are produced in the final or polishing stage of tumbling. A somewhat similar condition obtains in nature along the beach, either in the surf zone or in the quieter swash zone. We have found that polished pebbles on some present-day beaches in California bear small scratches with no preferred orientation. The turbulent action in a stream should also provide a certain freedom of motion, and smooth-surfaced pebbles from placer deposits are found to carry random, single striations.

Preferentially oriented microstriations.—To produce striations parallel to each other, the movements of the scratching agents in relation to the pebble must be unidirectional. The several processes discussed in the literature (tectonism, mass movement, wind, glacier, torrential stream flow, and ice jams on beaches or in streams) may satisfy these conditions to a greater or less degree. To this list we must add compaction as an additional process. Compac-

tion is capable of moving matrix around large particles such as pebbles, particularly if the matrix contains an appreciable amount of fine-grained material. This movement, if the matrix carries adequate abrasive material, should striate pebbles.

In considering the causes of the oriented microstriations described in an earlier section, several potential processes can be discarded. Thus, for various reasons, glacier ice, sea and river ice, wind, and mass movement are inappropriate to the particular microstriations described.

We have enough observations to suggest that both random and oriented striations can be produced in a stream environment. We have found that the random striations can be very small, but we have found no examples of true microstriations with preferred orientation resulting from stream action. Furthermore, we would expect that if oriented microstriations do form in a stream environment they would be formed in no particular chronologic sequence when compared with random microstriations. On the sets we have described here we find that, when the relative age of the microstriations can be determined, the sets of oriented microstriations are younger than the random microstriations. These considerations point to the conclusion that the oriented microstriations described in this paper were not formed in a fluvial environment but came into being subsequent to deposition.

We ascribe the systems of parallel microstriations described earlier either to tectonic movements or to compaction or to both. In the case of the pebbles from the Wapiabi formation other evidence points to tectonic activity, for some of the pebbles are pressure-pitted and all were collected from beds which have been folded and faulted. Compaction also may have played a role.

In considering the pebbles from the Cloverly, Morrison, and Windrow formations tectonic movements could also have been responsible, but there seems little to choose between this process and compaction. We are not able to explain the cause of the different sets of oriented striations on a single pebble, except to make the obvious comment that they show that the preferred direction of movement changed from set to set.

CONCLUSIONS

1. Microstriations, the largest of which are just visible to the naked eye, occur on some pebbles with smooth or polished surfaces.

2. Some striations are single scratches and occur randomly on the pebble. These can form in a tumbling machine, along a shoreline, and in a stream.

3. Other microstriations are arranged in parallel groupings. In some instances these microstriations define a coherent pattern over the entire pebble. In other cases they occur in two or more sets. Microstriations arranged parallel to one another on pebbles from the Wapiabi, Morrison, Cloverly, and Windrow formations are thought to be best explained by tectonism or compaction or both.

4. Microstriations may also be caused by ice jams in streams, by torrential stream flow, by wind-driven ice along a shoreline, by mudflows, or by glaciers.

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RELATIONSHIP BETWEEN CONCENTRIC LONGITUDINAL STRAIN AND CONCENTRIC SHEARING STRAIN DURING FOLDING OF HOMOGENEOUS SHEETS OF ROCKS

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ABSTRACT. In a folded sheet of rock which is homogeneous, isotropic, and behaves as a Newtonian medium, concentric shearing strain in the flanks, $\gamma_{\max}$, is shown to be related to maximum concentric longitudinal strains in the crest, $\epsilon_{\max}$, thus $\gamma_{\max}/\epsilon_{\max} = 2\pi \frac{D}{S}$. D is thickness of layer and S length of arc of one wave.

Unless thickness is larger than about one-third of the length of arc, diagonal shearing strain in the crests is shown to be greater than maximum concentric shearing strain in the flanks. For folded sheet with $\frac{D}{S}$ less than one-third, one should therefore expect to find traces in the form of fractures, slip planes, etc., in diagonal directions in the crests before such traces are detectable as concentric planes in the flanks.

If the folded layer is predisposed to concentric shearing by microscopic lamination or schistosity, the relation between maximum concentric shearing strain and maximum concentric longitudinal strain is found to be

$$\frac{\gamma_{\max}}{\epsilon_{\max}} = \frac{2D\pi\mu_c}{S\mu_t}$$

where μ_c is "effective viscosity coefficient" for concentric longitudinal strain and μ_t is "effective viscosity coefficient" for concentric shearing strain.

The relationships above refer to folds with small amplitude/wavelength ratio.

During plastic or viscous buckling of a sheet of homogeneous nonstratified rock, longitudinal as well as shearing strains occur parallel to the folded surfaces and perpendicular to the fold axis. One may refer to these strains as the concentric strains. Concentric longitudinal strain predominates in the crest of the folds where curvature is greatest, being compressive on the concave side of the neutral middle surface and extensive on the convex side. Concentric shearing strain predominates along the flank of the folds where curvature is at a minimum.

Although well aware of the presence of these kinds of strain in folded rock complexes, structural geologists do not seem to have attempted quantitative estimations of the relative significance of the two unlike strains as functions of thickness of layer, wavelength of folds, amplitude of folds, etc.

Without quantitative analyses of the situation it is impossible, for example, to take a stand with respect to de Sitter's ideas as expressed in his excellent book on structure (1959, p. 181, author's italics):

As I was personally convinced that this concentric folding (*i.e. by concentric shearing strain*) is also the predominating principle even when stratification does not predispose the material for this mechanism of folding

An experiment by de Sitter's co-worker, Kuenen, actually resulted in apparent concentric slip fractures in a folded piece of modeling clay. Does this mean that concentric shear in folded homogeneous rocks is common in nature

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and may perhaps give rise to concentric fracturing, lamination, and even concentric schistosity? Such conclusions based on a single experiment are premature, because analysis shows that shear of concentric type becomes predominant only when the thickness of a homogeneous nonstratified rock layer is great relative to the length of arc of the folds. A drawing of the experimental fold (de Sitter, 1959, p. 181) proves this point, for it shows indeed that the thickness was large relative to the length of arc.

In the analysis below we shall consider a homogeneous isotropic solid layer of even thickness that buckles to symmetric folds in response to a compressive force parallel to a direction in the plane of the original flat sheet. In order to prevent shearing strain parallel to the fold axis, and thus a kind of cross folding which does not concern us in this paper, we shall assume that the dimension perpendicular to the compressive stress and parallel to the fold axis is large relative to the length of arc of the folds. Assume moreover that the solid sheet has rheologic characteristics of highly viscous Newtonian substance, i.e. no yield point and rate of change of strain proportional to applied stress.

It is not strictly true that the deflection, y , of the neutral middle surface of the sheet under the stress conditions above is represented by a simple sine function

$$(1) \quad y = y_0 \sin \frac{2\pi x}{\lambda},$$

but an assumption to that effect will ease the consequent analysis considerably. In equation (1) y_0 is the amplitude of the fold, and λ its wavelength. The sine function gives a good approximation to the shape of the fold only as long as the amplitude/wavelength ratio is very small.

In order to estimate the concentric longitudinal and shearing strains, consider the sigmoidal-shaped segment $2h_0 ds$ in figure 1. The two quasi-radial sigmoidal curves which limit this segment are the distorted versions of two straight parallel lines which were normal to the surface of the sheet and separated by the distance ds_0 prior to folding. If concentric shear did not occur, the distorted segment would be limited by the stippled radial lines. The angle α is thus the shear angle at the neutral middle surface.

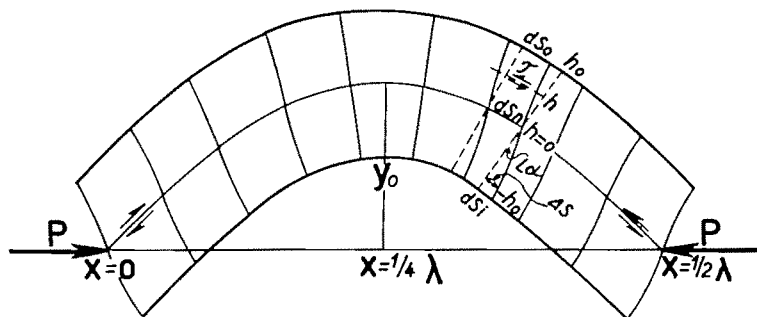


Fig. 1. Cross-section normal to x of a folded sheet of homogeneous viscous or plastic material. The sigmoidal curves across the sheet are the deformed versions of straight marker lines which were normal to the surfaces of the sheet prior to folding. The deflection, y , is considerably exaggerated relative to that studied in this paper.

When estimating the magnitude of the concentric longitudinal strain we may for a moment disregard the concentric shearing strain that is responsible for the sigmoidal shape of the segment. The fact that the distances ds_o , ds_n , and ds_l are different in length ($ds_o > ds_n > ds_l$) is due solely to the longitudinal concentric strain. The longitudinal concentric strain in the segment at

any distance h from the middle neutral surface is $\epsilon_h = \frac{ds_h - ds_n}{ds_n}$ which is

closely proportional to the distance from the neutral surface. In so-called pure bending (Timoshenko, 1940, p. 88) where concentric shear is nonexistent, it is strictly true that concentric longitudinal strain is proportional to distance from the neutral middle surface. When concentric shear varies along the arc, as it is proved to do in the present case, the above assumption of proportionality is not theoretically valid, although good enough to be employed in the theory of bending of beams (Timoshenko, 1940, p. 115). This approximation is also accurate enough for the purposes of the following discussion. During

the folding movement it is thus plain that the rate of change of strain, $\dot{\epsilon} = ds_h/dt$, is also closely proportional to the distance from the neutral surface. It follows that the longitudinal stress, σ , across any given radial section of the folded layer is proportional to the distance from the neutral surface because the relation between rate of change of longitudinal strain and corresponding

longitudinal stress in pure shear type of flow is $\sigma = 4\mu\dot{\epsilon}$ where μ is the coefficient of viscosity.¹ Equating the moment of the concentric longitudinal stresses at a given cross-section with the moment of the external compressive force results in

$$(2) \quad Py = 2 \int_{-h_o}^{h_o} \frac{\sigma_o}{h_o} h^2 dh = \frac{2}{3} h_o^2 \sigma_o$$

where P is the compressive buckling force reckoned per unit length in z dimension, and σ_o the concentric stress in the surface fibers, being positive at the convex surface and negative at the concave surface.

If the rate of change of concentric strain in the surface fibers is $\dot{\epsilon}_o = \frac{ds_o}{dt}$, which is related to the surface stress σ_o and the compressive force P , then

$$(3) \quad \dot{\epsilon}_o = \frac{\sigma_o}{4\mu} = \frac{3Py_o}{8\mu h_o^2} \sin \frac{2\pi x}{\lambda}, \text{ which is valid only}$$

for folds with small deflections.

The rate of change of concentric strain in any fiber at distance h from the neutral middle surface is

$$(4) \quad \dot{\epsilon}_h = \frac{3Py_o h}{8\mu h_o^3} \sin \frac{2\pi x}{\lambda}$$

as the strain is proportional to the distance from the central surface. In addi-

¹ It is assumed that stress normal to the layer is zero.

tion to showing that rate of change of concentric longitudinal strain vanishes at the neutral middle surface and reaches maximum value at the outer surfaces of the sheet, equation (4) also shows how $\dot{s}_h$ varies along the fold. $\dot{s}_h$ is zero at the points of inflection at $x = 0, \frac{1}{2}\lambda, \lambda, 1\frac{1}{2}\lambda$, etc., and reaches maximum values at the crest $x = \frac{1}{4}\lambda, \frac{3}{4}\lambda, \frac{5}{4}\lambda$, etc.

To estimate the magnitude of concentric shearing strain in the segment hds (fig. 1), consider the concentric shearing stress, τ_{sh} , at distance h from the neutral surface. This stress is equal to the net force which acts on the sides from h to h_0 of the segment divided by the area zds where z is the dimension of the fold parallel to the axis

$$(5) \quad \tau_{sh} = \int_h^{h_0} \frac{d\sigma_o}{ds} \frac{h}{h_0} dh = \frac{1}{2} \frac{d\sigma_o}{ds} \frac{(h_0^2 - h^2)}{h_0}.$$

For viscous shearing

$$(6) \quad \tau_{sh} = \mu \frac{d(\Delta \dot{s})}{dh} = \frac{1}{2} \frac{d\sigma_o}{ds} \frac{(h_0^2 - h^2)}{h_0}$$

where $\Delta \dot{s}$ is the rate of increment of the element Δs at the level h , and $\frac{d\Delta \dot{s}}{dh}$ is rate of change of shearing strain at level h . Equation (6) shows that at any given cross-section parallel to the fold axis of the layer (where $\frac{d\sigma_o}{ds}$ is a constant) shearing stress and rate of shearing strain vanish at the outer surfaces of the layer and reach maximum value at the neutral middle surface. This is opposite to the distribution of concentric longitudinal stress and strain as discussed above.

The rate of change of shearing strain at the neutral middle surface ($h = 0$) is

$$(7) \quad \dot{\gamma} = \left(\frac{d\Delta \dot{s}}{dh} \right)_{h=0} = \frac{1}{2\mu} \frac{d\sigma_o}{ds} h_0.$$

The rate of change of the element Δs is at the level h

$$(8) \quad \Delta \dot{s} = \frac{1}{2\mu} \frac{d\sigma_o}{ds} \left(h_0^2 h - \frac{1}{3} h^3 \right).$$

The magnitude of finite displacement Δs at any level h is proportional to the average rate of change of Δs at this level. Hence straight lines perpendicular to the flat sheet prior to the folding will be distorted to sigmoidal shape as given by equation (8) during folding. Incidentally this sigmoidal distortion is readily demonstrated by folding a sheet of modeling clay (see plate 1).

In order to determine how the concentric shearing varies along the fold, the differential quotient $d\sigma_o/ds$ in equation (7) must be evaluated. Differentiation of equation (3) results in

PLATE 1

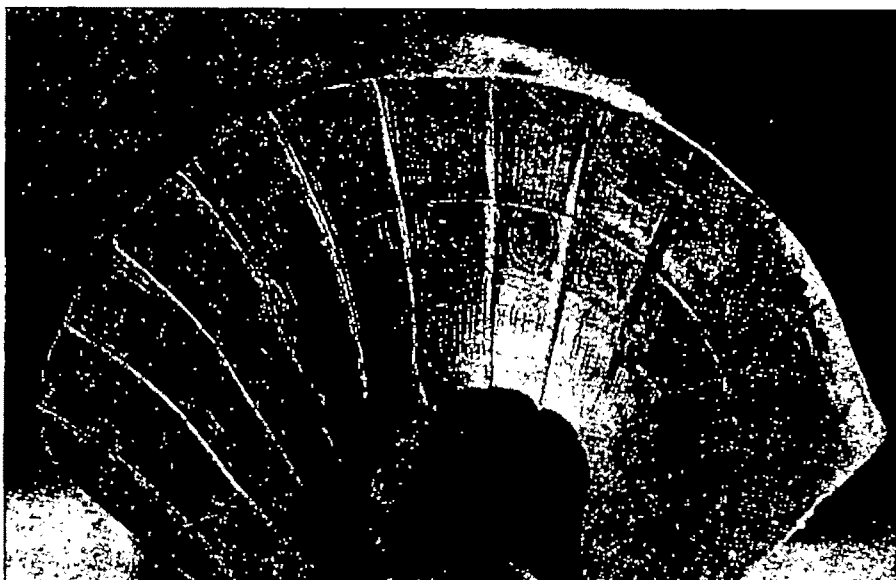


Photo of buckled sheet of plasticine. The sigmoidal curves are deformed marker lines which were straight and normal to the surfaces prior to buckling. The sigmoidal shape of the marker lines would have been even more pronounced if the uneven strain parallel to the fold axis (normal to the paper) could have been prevented.

$$(9) \quad d\sigma_o = 3 \frac{\pi P y_o}{h_o^2 \lambda} \cos \frac{2\pi x}{\lambda} dx.$$

The differential equation for length of arc of a curve expressed by the simple sine function (1) is

$$(10) \quad ds = \sqrt{1 + \frac{4\pi^2 y_o^2}{\lambda^2} \cos^2 \frac{2\pi x}{\lambda}} dx,$$

consequently the rate of change of concentric shearing strain along the neutral middle surface of the fold is

$$(11) \quad \dot{\gamma} = \frac{3 \pi P y_o \cos \frac{2\pi x}{\lambda}}{2\mu h_o \sqrt{\lambda^2 + 4\pi^2 y_o^2 \cos^2 \frac{2\pi x}{\lambda}}}$$

Rate of change of concentric shearing strain is then maximum at $x = 0, \frac{1}{2}\lambda, 1\lambda, 1\frac{1}{2}\lambda$, etc., and zero at $x = \frac{1}{4}\lambda, \frac{3}{4}\lambda, \frac{5}{4}\lambda$, etc.

$$(12) \quad \dot{\gamma}_{\max} = \frac{3 \pi P y_o}{2\mu h_o \sqrt{\lambda^2 + 4\pi^2 y_o^2}}.$$

To answer the question of relative importance of concentric longitudinal strain versus concentric shearing strain in folded layers of homogeneous rocks not predisposed to concentric shearing, and which behave as Newtonian sub-

stances, compare $\dot{\epsilon}_{\max} = \frac{3Py_0}{8h_0^2}$ (from eq. (3)) with $\dot{\gamma}_{\max}$ as given by equation (12)

$$(13) \quad \frac{\dot{\gamma}_{\max}}{\dot{\epsilon}_{\max}} = \frac{4\pi h_0}{\sqrt{\lambda^2 + 4\pi^2 y_0^2}}.$$

The term $(\lambda^2 + 4y_0^2\pi^2)^{1/2}$ does not differ substantially from the length of arc of a sinusoidal fold of shape $y = y_0 \sin \frac{2\pi x}{\lambda}$ as long as y_0 is less than say $1/20\lambda$. Hence

$$(14) \quad \frac{\dot{\gamma}_{\max}}{\dot{\epsilon}_{\max}} = 4 \frac{\pi h_0}{s} = 2\pi \frac{D}{s}$$

where s is the length of arc of one wave, and D is thickness ($=2h_0$) of the layer.

During buckling of a plastic sheet into concentric folds, thickness and length of arc remain substantially constant while wavelength and amplitude change. Thus the ratio between rate of maximum concentric shearing strain at the inflection lines at the flanks and rate of maximum longitudinal strain at the crests remains essentially invariant during evolution of the fold until the amplitude exceeds about one-twentieth of the wavelength. Consequently the ratio between finite maximum longitudinal strain and finite maximum shearing strain is also approximately equal to the constant $\frac{s}{4\pi h_0}$ at any moment as long as the deflection is small,

$$(15) \quad \frac{\gamma_{\max}}{\epsilon_{\max}} = 2\pi \frac{D}{s}.$$

Only when thickness is greater than $1/2\pi$ of the length of arc of a wave is the maximum shearing strain along the neutral middle surface on the flanks greater than maximum longitudinal strain at the surface fibers at the crests.

An interesting question for structural geology is to what extent concentric shearing strain (or stress) at the flanks is instrumental in developing any kind of concentric planar structural feature such as schistosity, cleavage, or slip planes in rocks not predisposed to such distortions. In considering this question it is pertinent to compare the concentric shearing strain on the flanks with the diagonal shearing strain associated with the concentric longitudinal strain in the crests (see fig. 2).

In pure shear type of strain, such as that occurring at the crest, finite maximum shearing strain is related to finite compressive strain along the principle axes as follows (see Jaeger, 1956, p. 29):

$$(16) \quad \gamma = \frac{1}{2} \left(\frac{1}{(\epsilon + 1)^2} - (\epsilon + 1)^2 \right)$$

where ϵ is finite compressive strain along the principal axis and γ is maximum finite shearing strain which makes an angle ϕ with the axis of compressive strain as determined by

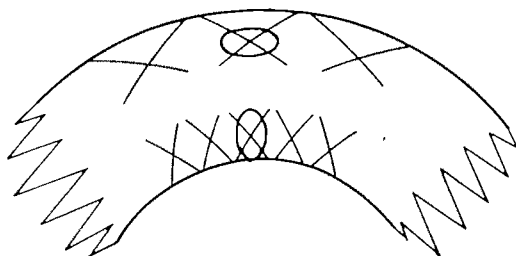


Fig. 2. Schematic indication of the directions of finite maximum shearing strain in the crest of a fold. The strain ellipses are indicated.

$$(17) \quad \operatorname{tg} \phi = \frac{1}{(\varepsilon + 1)^2},$$

(Jaeger, 1956). Figure 2 indicates the geometric relations of shearing and longitudinal strains in the crest of a fold.

According to equation (16) maximum finite shearing strain in pure shear type deformation is considerably greater in magnitude than the associated longitudinal compressive strain. Some corresponding values for ε and γ according to equation (16) are given in table 1. Unless the compressive strain is very large (numerically $> 1/2$), the corresponding shearing strain is numerically more than twice as large as the compressive strain.

TABLE 1

ε	-0.1	-0.25	-0.5
γ	0.21	0.63	0.91

On the other hand, equation (15) shows that concentric shearing strain on the flanks of a fold is numerically less than the longitudinal strain in the crest unless the layer is thicker than $\frac{1}{2\pi}$ of the length of arc. Thus diagonal shearing strain (and stress) in the crest is always greater than the concentric shearing strain (and stress) on the flanks for uniform layers whose thickness is less than about one-third of the length of arc of the fold.

The conclusion to be drawn from this is that if diagonal shearing cannot be traced in the form of slip planes, fractures, schistosity, etc., in the crests of gently folded uniform nonlaminated rock layers, there is no reason to believe that the weaker concentric shearing strain (and stress) in the flanks will manifest itself in the form of concentric slip planes, fractures, schistosity, etc., unless the thickness/length of arc ratio exceeds the critical value $1/\pi$.

In the discussion above we have disregarded the effect that deformations of rocks adjacent to the folded layer may have on the concentric shearing strain in the latter. It is particularly pertinent to the problem that, during the folding movement, adjacent incompetent rocks must flow away from the areas limited by the concave surface of the folded layer. Because of friction along

the contact this flow will increase the concentric shearing strain in the flanks. We shall not, however, attempt to treat this effect in the present paper.

Some laminated rocks are presumably predisposed to concentric shearing strain when affected by folding, because of less resistance to shearing parallel to the lamination than in any other direction. If the lamination is on a microscopic scale one may say that such rocks have anisotropic viscosity coefficient, the coefficient for shear parallel to the lamination being less than in any other direction. Denoting this minimum viscosity coefficient μ_t and the coefficient for concentric longitudinal strain in the crest μ_c , the relationship between finite maximum concentric longitudinal strain in the crest and finite maximum concentric shearing strain in the flanks becomes

$$(18) \quad \gamma/e = \frac{2\pi D \mu_c}{8\mu_t} (\text{from eqs. (3) and (12)}).$$

It follows that the smaller μ_t is relative to μ_c , the more pronounced the concentric shearing strain on the flanks relative to the concentric longitudinal strain in the crest and the associated diagonal shearing strain in this part of the fold.

The treatment of rocks as highly viscous Newtonian substance is, of course, somewhat questionable, although during microcreep (i.e. creep at stresses less than the "practical" yield point as measured in short-time tests) it is probable that rocks flow similar to viscous liquids in the sense that for long duration of small stresses they show no yield point. However, that rate of strain in rocks is directly proportional to magnitude of stress, as for a Newtonian substance, is less likely even during microcreep. Such probable deviation from the characteristics of a Newtonian substance makes the equations above less accurate descriptions of the various strains in folded rock layers. The important conclusion drawn from the equations is that concentric shearing strain on the flanks is insignificant relative to the strains in the crests for homogeneous rock layers unless the thickness/wavelength ratio is large. Does a possible deviation from Newtonian rheological behavior invalidate this conclusion? The answer will prove to be negative. For microcreep and slow recrystallization flow of the kind considered in this paper, rate of change of strain in rocks in all likelihood increases faster than linearly with increasing stress. This is shown by Griggs' experiment with wet alabaster, and it is also supported by thermodynamic theory (Griggs, 1940; Goranson, 1940). In other words the viscosity coefficient decreases with increasing stress. Work hardening is thus not significant during this kind of microcreep and recrystallization flow. The effect of this on the character of strains under folding of rock layers is to decrease the significance of the concentric shearing strain of the flanks relative to the strain in the crests. During folding of an isolated sheet of rock the stresses are greater in the crest than in the flanks (see eq. (2)); hence the effective viscosity coefficient, according to the conclusion above, is smaller in the crest than in the flank portions. Consequently the ratio between the rate of strain in the flanks and the rate of strain in the crests is actually less than that given by equation (15).

It is unfortunate that the mathematical analysis becomes rather cumbersome if the deflection of the folds exceeds the small magnitude considered in this paper. Under the stress conditions specified in the outset in this study, large-amplitude folds do not conform to a simple sine function, but rather to a shape similar to the so-called *elastica*s. A future paper will deal with an analysis of large-amplitude folds.

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THE NATURE OF MICROMETEORITES*

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ABSTRACT. (D. Hoffleit). The author believes that meteorite showers are usually caused by the fragmentation of one large meteorite in its rapid course through our atmosphere, rather than by the invasion of a swarm of initially discrete particles. In the process of fracture many small particles, including microscopic dust particles, must get separated from the main mass. These small particles have the fusion crust and morphological properties of meteorites in general. They differ from cosmic dust that enters the atmosphere directly from interplanetary space in that the cosmic dust particles are practically unaltered by impact with our atmosphere.

INTRODUCTION

A study of the morphological properties of meteorites leads to the conclusion (Krinov, 1955a, 1955b, 1958b) that during their movement through the Earth's atmosphere at cosmic velocity, meteoritic bodies as a rule break up into parts and fall to Earth as meteorite showers. Thus meteorite showers are due to the break-up in the atmosphere of individual meteoritic bodies and not to the invasion of the atmosphere by swarms of meteoritic bodies, as formerly believed (Krinov, 1956b).

The smallest fragments of such break-ups that have been examined reveal the morphological properties of larger meteorites.

MORPHOLOGICAL PROPERTIES

Among the individual samples collected after many meteorite showers, such as the Kainsaz, the Pultusk, and the Hesse, for example, there were minute samples that weighed a few grams or even a fraction of a gram (Prior, 1923). Extremely small samples weighing a fraction of a gram were likewise discovered in the region of the fall of the famous Sikhote-Alin iron meteorite shower. One of these remarkable microscopic meteorites has already been briefly described elsewhere (Krinov, 1955b, 1956a, 1956b, 1958a). Its dimensions are 5 x 4 x 3 mm and it weighs 0.18 gram. This micrometeorite was found as a black grain on a fallen tree leaf hanging on dry stubble (Krinov, 1952). Despite its small dimensions, it has clearly defined morphological properties typical of meteorites. It has a fused appearance, the characteristic regmagliptic relief, and is covered with a fusion crust. From the character of the surface of the micrometeorite its orientation in flight can be determined: the front end is convex and has a rather smooth surface (fig. 1), while the rear surface is slightly concave with a clearly defined regmagliptic relief (fig. 2).

Even smaller samples of the Sikhote-Alin meteorite shower were discovered in soil samples from the region of the fall. Of these the following four micrometeorites have the most clearly defined morphological properties characteristic of meteorites:

1. Diameter, 3mm; weight, 0.01 gram (fig. 3)

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2. Dimensions, 1.51 x 0.94 mm; weight, 0.0058 gram (fig. 4)
3. Dimensions, 1.51 x 0.68 mm; weight, 0.0021 gram (fig. 5)
4. Dimensions, 0.83 x 0.49 mm; weight, 0.0003 gram (fig. 6)

These micrometeorites are actually of microscopic dimensions in that their study, and particularly a morphological description of their properties, may be made only with the help of a binocular magnifying glass. The general fusion crust with its characteristic twinkling blue-gray luster, can be easily observed under a magnification of 30 to 40 times. The fusion crust is clear and easily noticeable even in the smallest micrometeorite, which weighs 0.3 milligram. Moreover, along the edges of the surface of this micrometeorite even the accumulation of crust is clearly visible (fig. 6). On the first of the above micrometeorites the well-defined regmagliptic relief and also the accumulation along the edges of the surface are easily seen (fig. 3).

In view of the characteristics of these minute meteorites it may be concluded that the term micrometeorites is fully applicable. Similar micrometeorites have been discovered in the region of the fall of other meteorite showers. For instance, after the fall of the Holbrook, U. S. A. stony meteorite shower on June 12, 1912, over 16,000 individual samples were collected. Among them, as Farrington (1915, p. 59) pointed out, over a thousand tiny samples were discovered no larger than a grape seed and weighing no more than several grams. Still smaller samples of this shower were discovered in an anthill by Nininger

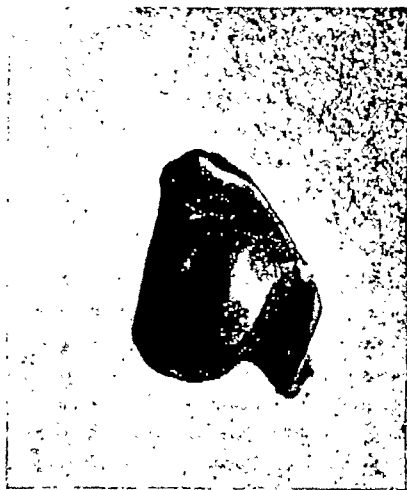


Fig. 1.



Fig. 2.

Fig. 1. One of the smallest individual samples of the Sikhote-Alin iron meteorite shower weighing 0.18 gram. The convex, front surface, which is more or less smooth. Magnified 7 times.

Fig. 2. The same sample as in figure 1, showing the rear surface with a clearly defined regmagliptic relief. Magnified 7 times.

(1952) in 1939 with the help of an alnico magnet. The following three were particularly well preserved and had clearly defined morphological peculiarities:

1. Dimensions, 2 x 2 x 3 mm; weight, 0.0183 gram
2. Dimensions, 2 x 2.5 x 3 mm; weight, 0.0248 gram
3. Dimensions, 2.5 x 3 x 4.8 mm; weight, 0.0518 gram

Each of these micrometeorites is entirely or almost entirely covered with fusion crust. In places where the accumulation of the crust has scaled, the typical gray inside matter of the meteorite is visible.

CONCLUSIONS

From the above it is obvious that the formation of micrometeorites is connected with the break-up of meteoric bodies in the atmosphere, as Nininger pointed out in 1952. Actually, each time a meteoric body breaks up, besides fragments of more or less large size, entire clouds of minute dustlike fragments fall on the Earth's surface as individual samples of meteorite showers. They become heated instantaneously and cause the phenomenon of sparks and the general flare of the bolide usually observed by eye-witnesses during its flight. The sparks are especially intense just before the bolide disappears, i.e. at the end of its visible trajectory or in the region of delay. It has been observed that, prior to their disappearance, bolides frequently split up into parts that spread out like a fan, accompanied by a cascade of sparks (Nielsen, 1953, fig. 10). The dust trains and individual cloud formations remaining after the flights of bolides (Nininger, 1952, pl. 2) probably consist of micrometeorites as well as solidified droplike globules (Krinov, 1958b), comprising the main mass of the train.



Fig. 3.



Fig. 4.

Fig. 3. A micrometeorite of the Sikhote-Alin meteorite shower, diameter 3 mm and weight, 0.01 gram. Shows the regmagliptic relief and the accumulation along the edges.

Fig. 4. The second micrometeorite of the same meteorite shower, 1.51 x 0.94 mm, weight 0.0058 gram. The general fusion and regmaglipts can be seen easily.

Thus, micrometeorites are minute fragments of meteoritic bodies which, having instantaneously become heated on the surface to melting, immediately drag and cool. As a result they become covered with the characteristic fusion crust and in general acquire the morphological properties typical of meteorites. The fall of meteorite showers must always be accompanied by micrometeorites, as it is impossible to imagine the break-up in the atmosphere of meteoritic bodies of any compositions known to us, without the formation of a considerable quantity of tiny fragments and dustlike particles. Most likely micrometeorites are also formed as a result of the partial break-up in the atmosphere of small meteoric bodies that invade the atmosphere from interplanetary space and cause the phenomena of bright meteors or weak bolides.

In both cases the micrometeorites formed become dispersed in the atmosphere by air currents and they steadily settle on the surface of the Earth and become mixed with the soil. Obviously this process of micrometeorite settlement is continuous and is more or less regular in time and space. There is probably a greater settlement of micrometeorites after, and in the area of the fall of meteorite showers, than during the period of intense meteor streams.

Although micrometeorites do possess the main features of meteorites, due to their small size, which is that of dust particles, they must be considered extraterrestrial dust and, the author believes, classed as one of the four forms now established (Krinov, 1955a, 1952; Krinov and Fonton, 1953).

In conclusion, I should like to touch upon the use of the term micrometeorite. First Whipple (1950, 1954) and then Fesenkov (1955) and others (Levin, 1956) showed that, because of their small size, the tiny cosmic dust-



Fig. 5.



Fig. 6.

Fig. 5. A third micrometeorite of the same meteorite shower, 1.51×0.68 mm, weight 0.0021 gram. The general fusion and the convex surface which is probably the front is clearly visible.

Fig. 6. The fourth micrometeorite from this same meteorite shower may be the smallest in the world, 0.83×0.49 mm, weight 0.0003 gram. The general fusion and accumulation along the edges (to the left at the bottom) can be seen.

like particles invading the Earth's atmosphere from interplanetary space drag before they are able to become heated. Consequently, such dust particles settle on the Earth's surface practically unchanged from their form in interplanetary space. Whipple and other researchers have named and now call such particles micrometeorites. As a result, this conception of micrometeorites is now widespread. However, as shown above, the term must be applied to the tiny particles of an entirely different nature which are the smallest fragments of meteoric bodies. Use of the term micrometeorite in reference to particles of cosmic dust is unfortunate, as these particles have not been subject to temperature changes and have not acquired the morphological properties characteristic of meteorites. It would, therefore, be more correct to call these particles cosmic dust, as the author has suggested (Krinov, 1958a, 1952; Krinov and Fonton, 1953).

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DISCUSSION

A PETROFABRIC ANALYSIS OF A FOLD

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In a recent paper Ball (1960) has presented the petrofabric analysis of a polygenetic fold. He concludes that a situation of shear followed by flexure has given rise to the final fold form. But it appears that his conclusion is not in perfect harmony with the data presented in the paper. For example, after partial unrolling, the patterns in the sectors 1 and 5 (Ball, fig. 7b) have not become identical as they should have been if the earlier form was entirely due to shear. Furthermore, the author suggests that in the fold core (sectors 2, 3, and 4) axial plane shearing has "sharpened the quartz fabric". If this be the case, for an extremely stress-sensitive mineral like quartz the present fabrics should be explained as solely due to this shear and should be homogeneous within this field (as they indeed are in the sectors 2, 3, 4, fig. 6b). So it is unlikely that the quartz fabrics in the sectors 2, 3, and 4 are inherited from the initial shearing pre-dating the final flexure and therefore should not be unrollable. Under these circumstances the identity of the fabric in the three sectors after partial unrolling must be explained as fortuitous.

What appears to be a more rational explanation of the features observed is given below. It is suggested that the fold form is due to flexure with concomitant shearing on the axial plane near the hinge. The symmetrical relationship of the quartz fabrics in sectors 1 and 5 probably indicates that the fabric evolved simultaneously with the main flexuring and is due to slip on the S_x plane consequent on flexuring. The direction-sense of slip on the two limbs is reversed and the patterns in the two limbs should be identical, but one is the mirror image of the other. Near the hinge the quartz fabric is due to axial plane slip and is homogeneous within this small field.

An alternative explanation may be that the fold is entirely flexural without any slip on the axial plane. The fabric patterns near the fold hinge represent the initial anisotropy of the quartz orientation prior to folding. Their preservation in the fold core is due to the fact that flexural slip is at a minimum near the hinge.

The above suggestions should be tested by more fabric analyses on the limbs and by dating the quartz with respect to deformation from petrographic evidences.

REFERENCE

Ball, T. K., 1960, A petrofabric analysis of a fold: *Am. Jour. Sci.*, v. 258, p. 274-281.

REPLY

A PETROFABRIC ANALYSIS OF A FOLD

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The discussion of my paper by Mukherjee raises some points which require clarification.

I concluded that shearing was followed by *accordion folding* (1960, p. 281) and not by simple flexure as suggested by Mukherjee. The similarity of quartz patterns in the sectors (fig. 6b) suggest a similar stress pattern for each. The mica fabric in the hinge of the fold indicates shearing subparallel with the axial plane. Assuming that the quartz fabric in the hinge of the fold (fig. 6) is related directly to this shearing couple, then it is difficult to relate a shearing couple about the S_x plane with the styles of quartz fabric exhibited in sectors 1 and 5.

REFERENCE

Ball, T. K., 1960, A petrofabric analysis of a fold: *Am. Jour. Sci.*, v. 258, p. 274-281.

ERRATUM

**PROPERTIES OF WATER. PART VI. ENTROPY
AND GIBBS FREE ENERGY OF WATER IN THE
RANGE 10-1000°C AND 1-250,000 BARS:**

A CLARIFICATION

CARL W. F. T. PISTORIUS* and W. E. SHARP**

Dr. William T. Holser of the La Habra Laboratory of the California Research Corporation kindly pointed out that the sources of the data used in the above paper (Pistorius and Sharp, 1960) were not made quite clear. Because the value of calculations such as the above depends to a large extent on the source material used, it was thought necessary to clarify the situation. The third paragraph of our paper should have read as follows:

"The specific volume of water has since been extensively remeasured in the range 1-1400 bars and 0-1000°C by Kennedy and his co-workers in a series

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of publications (Kennedy, 1957; Kennedy, Knight, and Holser, 1958; Holser and Kennedy, 1958; Holser and Kennedy, 1959). A compilation made by Kennedy and Holser in 1957, but not yet published, was corrected within that range where necessary to conform with these latest measurements. Outside of that range, the following data had been smoothed for that compilation:

1,600- 10,000 bars	-10°- 80°C	Bridgman (1912) as recomputed by Goranson (1942);
1,600- 10,000 bars	90°- 100°C	Bridgman (1931, 1935);
1,600- 2,500 bars	380°- 600°C	Kennedy (1950) corrected and smoothed to conform with recent data;
1,600- 2,500 bars	600°- 800°C	Extrapolated on isometrics;
5,000- 25,000 bars	200°-1000°C	Interpolated
25,000-250,000 bars	200°-1000°C	Rice and Walsh (1957);
5,000- 50,000 bars	80°- 180°C	Bridgman (1942).

The corrected compilation was used in the following calculations."

NEW REFERENCES

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REVIEW

Geology for Engineers, 2nd ed.; by JOSEPH M. TREFETHEN, P. 632; 241 figs., 63 tables, 2 appendices. Princeton, 1959 (D. Van Nostrand Company, \$8.50).—After seven successful reprintings of the widely used text, *Geology for Engineers*, a revision is indeed timely. The presentation, format, and illustrations are essentially the same as in the first edition. Dr. Trefethen has strengthened parts of the text considerably by incorporating new subjects and up-dating the coverage of several chapters. However, some deserving chapters still lack sufficient revision.

This text is designed for the engineering student or practicing engineer who seeks an introduction to geological science together with some practical engineering applications. The text does not pretend to be an advanced treatise or a reference for trained geologists, but rather provides an insight into the manner in which the services of a qualified geologist are utilized in civil engineering and specialized branches thereof. Certain complex geologic principles combined with some common engineering problems have been discussed with admirable clarity and simplicity.

The first four chapters dealing with minerals, rocks, and igneous activity emphasize the physical properties of natural materials, a basic background for the practicing engineer. The author then proceeds to demonstrate the technique of analyzing purely descriptive geologic information to supply a quantitative answer for engineering.

Three chapters deal with the processes that affect the strength and properties of rocks, such as "Rock Weathering" with the resultant development of sediments and soils. This phenomenon, often slighted in a discussion of geologic features, is of fundamental importance to the soils or foundation engineer. The steps from rock to soil are traced in a smooth and understandable sequence which is a signal feature of this text.

The topic of "Geologic Structures" is inter-related with that of "Earthquakes" and a partial introduction to engineering seismology. The brief chapter on "Geologic Field Work" merely summarizes the simple methods of collecting field data and the type of instruments usually employed. No attempt is made to discuss the interpretation of field data or the presentation of the information, both aspects being outside the scope of this text.

The remaining part of this new edition begins with a brief summary of the Earth's history, which is followed by additional principles and applications exemplified by the eight successive chapter titles: "The Atmosphere", "Subsurface Water", "Earth Movements", "Streams", "Dam Sites and Reservoirs", "Shorelines", "The Work of Glaciers" and "Geologic Interpretation of Topographic Maps and Airplane Photographs". These principles are clearly presented and useful examples are smoothly integrated. For instance, the discussion on interpretation of geologic maps, extensive for this type of a text, indexes the significance of important phenomena as illustrated on maps to appropriate engineering applications.

Chapters that have been substantially strengthened in the revised text are: "Minerals", "Subsurface Water", "Streams", and "Unconsolidated Sediments". These sections should prove to be popular with both the student and instructor. Chapters such as "Unconsolidated Sediments" and "Weathering"

are excellent background for the student who subsequently embarks on a more advanced study of natural materials, soil mechanics, and foundation engineering.

Of questionable value, however, is the chapter on "Introduction to Geophysical Techniques", particularly as other exploration methods of the geologist, such as drill holes and man-sized openings, are not discussed. The chapter on "Earth Movements", although broadened in the revision, follows an early classification that could be substantially strengthened by inclusion of the extensive classification of 1958 by the Highway Research Board. The set of geologic symbols used in the section on maps is not the accepted representation of the profession; no explanation is offered for utilizing this system.

A text on geology in engineering must of necessity be international in scope. References on several subject areas should therefore be up-dated to include outstanding recent works, as in engineering seismology, dam sites and reservoirs (latest listed here, 1951) and rock properties. A notable omission is the lack of references on rock mechanics, an applied phase of structural geology which has been widely studied in the past decade. As a consequence, Appendix II, a partial coverage on the physical properties of rocks, is of limited usefulness only.

This text is recommended for the introduction of basic geologic principles to engineering students and professionals alike. *Geology for Engineers* will undoubtedly continue to be a favorite and well accepted.

GEORGE A. KIERSCH

Publications Recently Received

Physical Geography, 2nd ed.; by Arthur N. Strahler. New York, 1960 (John Wiley and Sons, Inc., \$7.50).

Principles and Procedures of Statistics; by Robert G. D. Steel and James H. Torrie. New York, 1960 (McGraw-Hill Book Co., \$10.50).

The Geographical Fragments of Hipparchus; edited by D. R. Dicks. New York, 1960 (Oxford University Press, \$7.20).

Elements of Crystallography and Mineralogy; by F. Alton Wadwe and Richard B. Mattox. New York, 1960 (Harper and Brothers, \$7.50).

Invertebrate Paleontology; by William H. Easton. New York (Harper and Brothers, \$10.00).

American Journal of Science

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THE ZEOLITE FACIES: AN INTERPRETATION*

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ABSTRACT. The zeolite facies, formed under conditions intermediate between diagenesis and regional metamorphism, is characterized by mineral assemblages bearing laumontite, heulandite, or analcite, together with quartz. If H_2O and CO_2 are regarded as mobile components, these assemblages, under the same conditions, rule out the following: calcite-kaolinite-quartz, calcite-pyrophyllite-quartz, or albite-quartz; these assemblages are all familiar in sediments, sedimentary rocks, or low-grade regional metamorphic rocks.

The relations among these alternative assemblages are analyzed by means of isothermal, isobaric diagrams using as variables the chemical potentials of the two mobile components, H_2O and CO_2 . For a given reaction, it is not only possible to arrange correctly the relative dispositions of the pseudo-univariant lines around pseudo-invariant points, but also to assign numerical values to the slopes of the pseudo-univariant lines on the basis of the stoichiometric coefficients of the two mobile components. Such diagrams show that mineral assemblages of the zeolite facies can be obtained, isothermally and isobarically, by increasing the chemical potential of H_2O relative to that of CO_2 . Thus the zeolite facies is not a necessary intermediate step between diagenesis and regional metamorphism.

Fyfe, Turner, and Verhoogen (1958, p. 167) urged the establishment of a new metamorphic facies at the low-grade end of the metamorphic spectrum. This facies is characterized by zeolites such as laumontite, heulandite, and analcite, and is called by these authors the zeolite facies. The petrographic evidence for mineral assemblages of regionally metamorphosed rocks, characterized by zeolite, is based largely upon the detailed study of Coombs (1954) on the altered Triassic sediments of Southland, New Zealand. Recently Coombs, Ellis, Fyfe, and Taylor (1959) supplied more data, both petrographic and experimental, on zeolitic assemblages and their stability ranges; these authors also reviewed the existing data on the occurrences of zeolitic metamorphic rocks. The reality and importance of zeolite-bearing mineral assemblages in regionally metamorphosed rocks seem well documented.

Fyfe, Turner, and Verhoogen (1958, p. 167, 201) state that the zeolite facies occurs under conditions of lower temperature and pressure than the greenschist facies, which is characterized by such mineral assemblages as quartz-albite-muscovite-chlorite. These authors suggest that the zeolite facies occurs between common sediments and the greenschist facies of metamorphism. In view of the rather extensive record of mineral assemblages which do not bear zeolites, in rocks ranging from sediments (Revelle, 1944; Neeb, 1943; Zen, 1959a, 1959b) to sedimentary rocks (Potter and Glass, 1958; Millot, 1950; Ostrom, 1959; Ehlmann, 1958; Robbins and Keller, 1952; Grim, Lamar, and Bradley, 1937; Grim, Bradley, and White, 1957; Lippmann, 1955), however, such a facies is almost certainly not a necessary intermediate stage of rock metamorphism. The writer recently also observed (Zen, 1960) that, in the Champlain Valley-Taconic Range area of western Vermont at least,

* Publication authorized by the Director, U. S. Geological Survey.



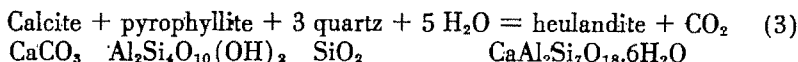
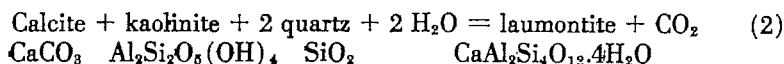
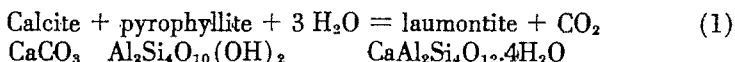
metamorphic assemblages characteristic of the greenschist facies merge imperceptibly into apparently unmetamorphosed sedimentary rocks without the occurrence of any zeolite.

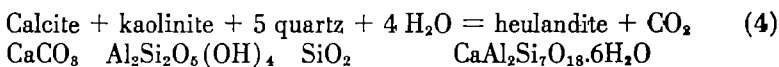
Clearly two different trends of metamorphic evolution are indicated. To explain the observations, however, it is desirable to consider more independent variables than just temperature and/or total pressure; for although Fyfe, Turner, and Verhoogen (1958, p. 167, 201) and also Coombs and others (1959, p. 54, 60) imply that the zeolite facies is separated from the greenschist facies by differences in temperature and/or total pressure, the definition of a metamorphic facies should depend on the entire set of independent and externally imposed physicochemical variables (Thompson, 1955, p. 66) as reflected in differences in mineral assemblages. Under ordinary conditions, the most significant of the variables besides temperature and total pressure are the externally controlled values of the chemical potentials of mobile components. It is the purpose of this paper to call attention to this fact and also to offer a possible interpretation of the zeolite facies.

As the only general description of rocks belonging to the zeolite facies is for the area in New Zealand, Coombs' descriptions and data will be used extensively.

From the study of Coombs (1954) and Coombs and others (1959), it appears that the phases most typical of the zeolite facies are laumontite, heulandite, and analcite, all found typically with quartz. These phases have the ideal compositions, respectively, of $\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$, $\text{CaAl}_2\text{Si}_7\text{O}_{18}\cdot 6\text{H}_2\text{O}$, and $\text{NaAlSi}_3\text{O}_8\cdot \text{H}_2\text{O}$. This paper discusses only the reactions involving the calcic zeolites, laumontite and heulandite, and will use the above ideal formulas for these minerals. The argument can be easily extended to analcite-bearing assemblages. The use of ideal formulas would not affect the general discussion; modifications necessary for nonstoichiometry of the phases will be briefly considered later.

In many sediments and sedimentary rocks, the assemblage calcite-kaolinite-quartz is known (Zen, 1959a, 1959b; Millot, 1950; Ostrom, 1959; Ehlmann, 1958; Potter and Glass, 1958; Grim, Lamar, and Bradley, 1937; Keller and Ting, 1950; Robbins and Keller, 1952). The assemblage calcite-pyrophyllite-quartz has also been reported from shales of the Mississippian Manning Canyon formation in Utah (Ehlmann, 1958, p. 21, 37, 61). These assemblages are related to the laumontite-quartz and heulandite-quartz assemblages by the following reactions, using ideal formulas for the zeolites given by Coombs and others (1959, p. 61):





Of the four reactions, at arbitrary values of T and P , no more than three can be stable, and the fourth one must involve metastable equilibrium as the reactions are not all independent of one another.

All four reactions involve two volatiles, H_2O and CO_2 . If these are mobile components, with their chemical potentials externally controlled, then variations in their values may be used in the same manner as variations in temperatures and pressure in defining metamorphic facies through the different mineral assemblages. It is therefore of interest to plot the reactions as functions of these chemical potentials, $\mu_{\text{H}_2\text{O}}$ and μ_{CO_2} , at some arbitrary temperature and pressure, so chosen as to be of interest in our problem. (A plot such as this one can of course be made even where H_2O and CO_2 are not mobile components. However, if these two components are inert, then the values of their chemical potentials are determined by initial concentrations rather than independently variable. Thus they cannot be used to define metamorphic facies.) In this plot, assuming all solid phases to have constant compositions, it is possible to assign numerical values to the slopes of the univariant lines (univariant at fixed temperature and pressure; actually trivariant) as can be easily demonstrated.

In a general reaction $\nu_A A + \nu_B B + \dots = \nu_R R + \nu_S S + \dots$, we have, for each phase γ , the Gibbs-Duhem relation,

$$-S^\gamma dT + V^\gamma dP - \sum_i (n_i d\mu_i)^\gamma = 0$$

where n_i is the total number of moles of component i in phase γ . The expression, at constant temperature and pressure, reduces to

$$\sum_i (n_i d\mu_i)^\gamma = 0$$

Let us sum all such expressions for the solid phases and all components i for each side of the reaction. Such sums must remain equal to zero, since each phase is in internal equilibrium:

$$\sum_{\gamma} \sum_i (n_i d\mu_i)^\gamma = 0$$

Along the univariant curve representing the reaction, $\Delta G = 0$; moreover the values of all the μ_i 's for each component must be the same in all phases. Therefore we have

$$\sum_i n_i^{\text{total}} d\mu_i \Big|_{\text{left side}} = \sum_i n_i^{\text{total}} d\mu_i \Big|_{\text{right side}}$$

and

$$\sum_i \Delta n_i d\mu_i = 0$$

where

$$\Delta n_i = n_i^{\text{right}} - n_i^{\text{left}}$$

For inert components, $\Delta n_i = 0$ so that we are left with

$$\sum_{i=\text{mobile}} \Delta n_i d\mu_i = 0$$

If two mobile components participate in the reaction, we have

$$\Delta n_1 d\mu_1 + \Delta n_2 d\mu_2 = 0$$

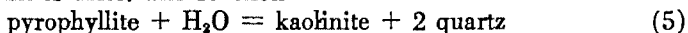
and

$$(\partial\mu_1/\partial\mu_2)_{T,P,\Delta G=0} = -\Delta n_2/\Delta n_1$$

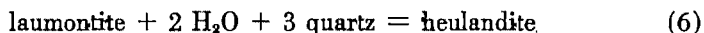
Now these quantities, Δn_1 and Δn_2 , are equal to the number of moles of volatiles evolved in our general reaction. If the volatiles appear on opposite sides of the equation, Δn_1 and Δn_2 have different signs; therefore the slopes of the univariant lines are just the inverse of their stoichiometric ratios in the fluid phase for the particular reaction. A similar equation has been given by Korzhinskii (1959, p. 97, 119)¹ by a slightly different method of derivation.

This knowledge, coupled with the condition that a phase assemblage cannot be both stable and metastable in a given divariant field,² enables us to draw topologically correct phase diagrams in the $\mu_{H_2O} - \mu_{CO_2}$ projection.

Two possibilities arise. The reaction



may occur at a lower value of μ_{H_2O} than the reaction



or the reverse may be true. Since we have as yet no data to decide which combination occurs in nature, both alternatives are constructed and shown in figure 1A (μ_{H_2O} for reaction 5 lower than for reaction 6) and figure 1B (the converse case). The figures were drawn so that only mineral assemblages including quartz are considered. For assemblages without quartz, the diagrams become much more complex and their construction does not seem justified at this time. With ubiquitous quartz, the system becomes pseudo-binary (in addition to the mobile components CO_2 and H_2O); the possible assemblages can

¹ H. P. Eugster pointed out an alternative derivation of this relation (written communication). For a reaction in which all the solids have fixed compositions, and in which one or more of the components are volatiles, we have

$$\ln K = \ln \prod_i a_i^{\nu_i} = \sum_i \nu_i \ln a_i$$

where a_i is the chemical activity and ν_i the stoichiometric coefficient of component i in the reaction, and where the sign of ν_i is determined by the side of the reaction equation in which it occurs. Substituting the relation

$$\mu_i = \mu_i^\circ(T, P) + RT \ln a_i$$

and differentiating both sides at constant T and P (thus taking the volatile components to be mobile components), we get

$$0 = \sum_{i=\text{mobile}} \nu_i d\mu_i \Big|_{T,P,\Delta G=0}$$

² This statement, which is obviously true, implies that angles between stable portions of neighboring lines must be no greater than 180° (Morey and Williamson, 1918, p. 65-66). In addition, in a general case, apart from an ambiguity of clockwise versus counterclockwise progression of univariant curves (Niggli, 1954, p. 408), it also suffices to fix uniquely the relative locations of divariant assemblages. Thus, for example, in a binary system with four phases there are four univariant curves emanating from an invariant point. The stated condition requires that the divariant field in which all four phases are intrinsically stable must contain no metastable extension of univariant curves; the two divariant fields in each of which three phases are stable must each contain the metastable extension of one univariant curve, and the divariant field in which only two phases are stable must contain two metastable extensions of univariant curves.

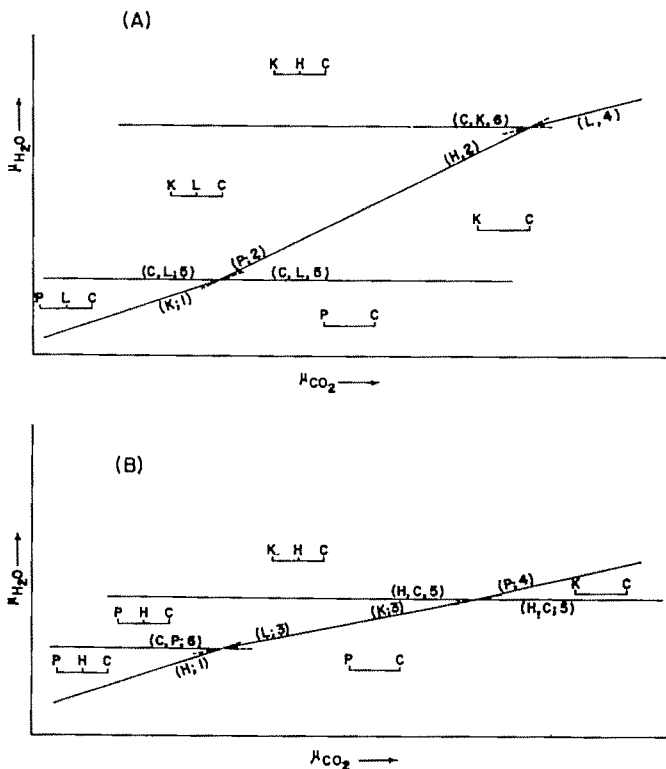


Fig. 1. The system $CaO-Al_2O_3$ in the presence of quartz and at some arbitrary value of temperature and total pressure, as function of the chemical potentials of CO_2 and H_2O . (A) value of μ_{H_2O} assumed to be higher for laumontite breakdown than for pyrophyllite breakdown; (B), the converse case. Abbreviations: K, kaolinite; P, pyrophyllite, H, heulandite; L, laumontite; C, calcite. Symbols in parentheses give the phases absent in each univariant equilibrium; numerals in parentheses give the numbers of the describing equations in the text. Compositional degeneracy is indicated by two symbols appearing together in a parenthesis. Short lines with symbols above give the mineral assemblages in each pseudo-bivariant field, projected from the SiO_2 (quartz) apex to the $CaO-Al_2O_3$ binary boundary (PHC in bottom left field of B should read PLC).

then be shown for each pseudo-bivariant phase field along a single compositional coordinate, the $CaO-Al_2O_3$ binary, as given in the figures.³

For a binary system, an invariant point is a quadruple point from which four univariant lines normally emanate. Of the two invariant points in each of figures 1A and 1B, however, one has only three radiating univariant lines. This is due to the compositional degeneracy of the system in the lime-alumina-silica projection: ignoring H_2O and CO_2 , pyrophyllite-kaolinite-quartz, laum-

³ Although montmorillonite is common in the zeolite-bearing rocks described by Coombs (1954) and Coombs and others (1959), this phase is not considered here, because natural montmorillonites generally do not belong to the simple system here considered. Even if it were included in the system, no fundamental revision of our conclusions will result, except that since montmorillonite is a H_2O -rich phase, carbonate-clay mineral assemblages including it will have larger stability fields in the μ - μ plot than those without; correspondingly the sizes of fields of zeolitic assemblages will shrink.

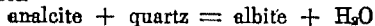
ontite-heulandite-quartz, and calcite-laumontite-pyrophyllite are colinear phases. Where the stable portions of two univariant curves involving these degenerate phases coincide (the situation where the compositions of the non-participating phases lie on opposite sides of the line of the degenerate phases), a single curve terminating at the invariant point results; where the stable and metastable portions of the univariant curves coincide (compositions of non-participating phases lie on the same side of the line of the degenerate phases), a single curve with continuous slope passes through the invariant point (Morey and Williamson, 1918, p. 69; Morey, 1957, p. 464; for a less mathematical discussion, see Niggli, 1954, p. 413). In figure 1, the fact of degeneracy is manifested by the identity of the missing phases along each univariant line, given in parentheses.

The slopes of the lines will be affected by changing contents of zeolitic water with changing values of $\mu_{\text{H}_2\text{O}}$. This certainly happens; unfortunately we cannot as yet evaluate this effect quantitatively. It is clear, however, that for reactions involving both CO_2 and H_2O , rising values of $\mu_{\text{H}_2\text{O}}$ will cause the slopes to flatten due to increasing amounts of zeolitic water, either continuously or in discrete steps if the zeolitic water changes in discrete amounts as does the water of montmorillonite (Bradley, Grim, and Clark, 1937). For the reaction going from laumontite to heulandite (reaction 6), the effect will be to shift the horizontal univariant line up and down the $\mu_{\text{H}_2\text{O}}$ coordinate. The general appearance of figure 1, however, will not be affected, except in so far as new pseudo-invariant points involving first-order transitions of different hydrates of the zeolites must be added.

Natural laumontite, but even more so natural heulandite (Coombs and others, 1959, p. 101), show compositional variabilities other than in their H_2O content. For example, sodium could substitute for calcium with concomitant substitution of silicon for aluminum. On the $\mu_{\text{H}_2\text{O}} - \mu_{\text{CO}_2}$ plot, reaction (6) therefore should be represented by a band, rather than a line. If, however, a sodic phase such as analcite or albite occurs (Coombs, 1954, p. 84, 86, 87, 90), the chemical potential of sodium is buffered and the band again reduces to a line* in the particular projection of the multicomponent system.

The mineral assemblage calcite-kaolinite-quartz has been well documented, both in modern sediments and sedimentary rocks of all ages, in references already cited. The assemblage calcite-pyrophyllite-quartz is reported by Ehlmann (1958). The assemblage laumontite-calcite-quartz is reported by Coombs and others (1959, p. 63), and also by W. S. White of the U. S. Geological Survey (1960, oral communication) from the amygdules in basalt of the Michigan copper deposits. The assemblage calcite-heulandite-quartz is reported by Coombs (1954, p. 86). The writer can find no data on calcic zeolite-kaolinite or calcic zeolite-pyrophyllite assemblages. Coombs (1954, p. 81) reports kaolinite in the altered Triassic rocks of New Zealand, but not specifically associated with zeolite. W. S. White (1960, oral communication) also finds

* Similarly for the reaction



if the analcite is nonstoichiometric but contains potassium, the presence of a potassic feldspar will remove the difficulty of graphical representation.

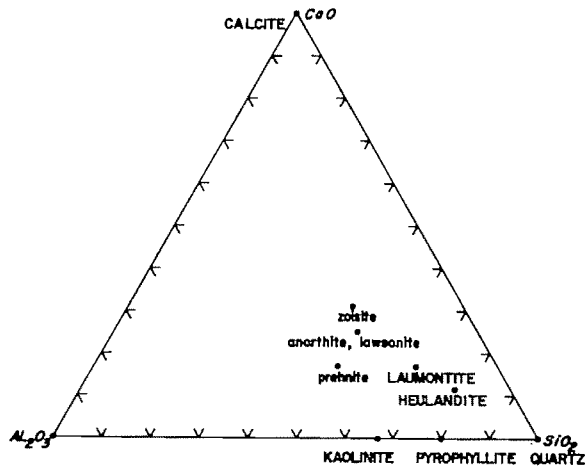


Fig. 2. The $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ projection of the chemical compositions of minerals pertinent to the present discussion, calculated in terms of the formula ratios (for laumontite and heulandite, the compositions given in the text are used). Note that in this projection the following phases are compositionally degenerate: quartz-heulandite-laumontite; quartz-pyrophyllite-kaolinite; calcite-laumontite-pyrophyllite; calcite-zeolite-anorthite-lawsonite-kaolinite.

laumontite and kaolinite in the same general sequence of strata in Michigan, but so far these have not been found together. Pyrophyllite-clinozoisite-quartz (Stuckey, 1926; Zen, 1961) has been found, but this association clearly shows (fig. 2) that conditions of metamorphism were such that heulandite and laumontite were intrinsically unstable. It thus appears impossible at the moment to choose between figures 1A and 1B on petrographic evidence. As laumontite has not been synthesized so far (Coombs and others, 1959, p. 88), and the kaolinite-pyrophyllite transition has not been established, laboratory data are of no help here.⁵

The above discussion assumes the validity of the suggestion by Coombs and others (1959, p. 60) that such phases as prehnite and zeolite do not overlap heulandite and laumontite in their stability ranges. Figure 2 shows that prehnite-bearing assemblages and the zeolites are mutually exclusive where, for instance, the assemblage prehnite-calcite-quartz is stable. However, the stability range of prehnite alone is wider than that of prehnite-bearing assemblages. It is thus quite conceivable that such assemblages as laumontite-prehnite-quartz or even heulandite-prehnite-quartz are stable under certain conditions. Such assemblages would exclude heulandite-kaolinite, heulandite-pyrophyllite, laumontite-kaolinite, and laumontite-pyrophyllite assemblages under the same conditions, and would explain why these are not found. It is hoped that petrographic data may soon be available to settle this question.

Notwithstanding these gaps in our knowledge, it appears that at constant temperature and pressure, it is possible to obtain, for a system isochemical

⁵ See, however, the following paper which appeared after this manuscript went off to the press: Carr, R. M., and Fyfe, W. S., 1960, Synthesis fields of some aluminum silicates, *Geochim. et Cosmochim. Acta*, v. 21, p. 99-109.

with respect to the inert components, both mineral assemblages characteristic of the zeolite facies and of the greenschist facies, depending on the relative values of μ and $\mu_{\text{H}_2\text{O}+\text{CO}_2}$. At high values of $\mu_{\text{H}_2\text{O}}$ and low values of μ_{CO_2} , the zeolite facies prevails; however many sediments and sedimentary rocks evidently did not recrystallize under these conditions. Relative values of μ_{CO_2} are commonly high enough so that the alternative assemblages, calcite-kaolinite-quartz or calcite-pyrophyllite-quartz, obtain. Similarly, many rocks show diagenetic development of albite-quartz, albite-muscovite-potassic feldspar-quartz, and possibly also albite-muscovite-kaolinite-quartz (Zen, 1960, p. 152). Such assemblages rule out the zeolitic analcite-quartz assemblage under the same conditions.

Rising temperature and total pressure may or may not favor the non-zeolitic assemblages, depending on which independent variables are held constant. Thus, consider the changes in total Gibbs Free Energy for reactions (1) through (4), proceeding to the right:

$$\begin{aligned}(\partial \Delta G / \partial T)_{P, \mu} &= -\Delta S_s \\(\partial \Delta G / \partial T)_{P, a} &= -\Delta S_s + \nu_{\text{H}_2\text{O}} [S^\circ - R \ln a]_{\text{H}_2\text{O}} \\&\quad - \nu_{\text{CO}_2} [S^\circ - R \ln a]_{\text{CO}_2} \\(\partial \Delta G / \partial P)_{T, \mu} &= \Delta V_s \\(\partial \Delta G / \partial P)_{T, a} &= \Delta V_s + \nu_{\text{CO}_2} V^\circ_{\text{CO}_2} - \nu_{\text{H}_2\text{O}} V^\circ_{\text{H}_2\text{O}}\end{aligned}$$

The subscript "s" denotes solid phases, and the symbols μ and a in the subscripts apply to all mobile components. Activity is so defined that the standard state is the pure component in its stable state at the particular temperature and total pressure. If the mobile components behave ideally, the right-hand sides of expressions 2 and 4 above simply reduce to the total entropy and volume changes, respectively. In any case, the departure from ideality is probably small, and ideal-mixture approximations remain useful.^a

The expressions 1, 2, and 4 cannot be evaluated even as to sign, because of insufficient data. In particular, entropies of the zeolites are needed to evaluate expression 1. In addition, we need to know the state of aggregation of the mobile components in order to evaluate the second and fourth expressions. Expression 3 is the only one for which quantitative data are available. Using a density of about 2.3 for laumontite and 2.2 for heulandite (Coombs and others, 1959, p. 101), the volume changes for reactions (1) through (4) to the right are, respectively, + 42 ml, + 24 ml, + 83 ml, and + 65 ml.

Under the conditions stipulated in expression 3 above, therefore, an increase in total pressure will favor the nonzeolitic assemblages. In general, however, it is unsafe to conclude that temperature and pressure increases favor the nonzeolitic assemblages unless the conditions and processes have been carefully investigated. On the other hand, our preceding discussions do show that at constant temperature and total pressure, changes in the chemical potentials of the mobile components, H_2O and CO_2 , could account for the different trends of metamorphism.

^a I am indebted to J. B. Thompson for calling my attention to the need of discrimination between these two sets of conditions in this discussion.

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PLEISTOCENE GEOLOGY AND PALEONTOLOGY OF THE TALARA REGION, NORTHWEST PERU

R. R. H. LEMON¹ and C. S. CHURCHER²

ABSTRACT. Three major erosion surfaces (Tablazos) and associated deposits of Pleistocene age in coastal northwestern Peru are described. The marine deposits are richly fossiliferous; the Mancora (oldest) and Talara tablazo faunas are of cooler-water type, the Lobitos (youngest) fauna is similar to that of the modern shoreline.

A terrestrial vertebrate fauna from tar seep deposits on the Mancora Tablazo is similar to that of the Carolinian of Ecuador. A provisional list of the Talaran fauna is compared with faunas from the Carolinian of Ecuador and from Rancho La Brea, California.

It is likely that the local climatic regime of the coastal plain differed little from that of the present day. However, the tar seep fauna suggests an at least moderately abundant water supply, probably provided by permanent or semi-permanent streams rising in a wetter hinterland.

INTRODUCTION

The coastal region of northwestern Peru is underlain by extensive Pleistocene marine sediments containing a rich shelly fauna. Little detailed work has been done in the area, although Bosworth (1922) gave an account of the Pleistocene deposits. The interest of this region is further enhanced by the presence of surface tar seeps containing a varied vertebrate fauna of Pleistocene age.

A study of the tar seeps and associated deposits and of the Pleistocene geology of the area in general was made by Lemon, while extensive excavation and careful screening of the most richly fossiliferous parts of the brea deposits was carried out by A. G. Edmund and R. R. Hornell of the Royal Ontario Museum.

Laboratory preparation and study of the brea material is now being undertaken by A. G. Edmund and C. S. Churcher. The present paper is intended as a preliminary account only, and the conclusions reached may be subject to modification as work progresses.

PRE-PLEISTOCENE GEOLOGY

The oldest rocks occurring in the area are quartzites, graywackes, argillites, and shales of the Pennsylvanian Amotape formation. They outcrop over extensive areas in the Amotape Mountains to the east and have been recognized in subsurface. The sediments have been intruded by granites in some areas and are usually considerably faulted and brecciated. The total thickness is in excess of 4600 feet.

Unconformably overlying the Amotape formation are sediments ranging from Aptian to Albian in age. These outcrop in a small fault block in the extreme east of the present area and elsewhere are known in subsurface. The lower beds include reef limestones and thin-bedded black limestones, but the greater part of the section consists predominantly of shales with associated sandstones and conglomerates. The youngest beds pass up into sandstones and shales of Lower Eocene age.

The Cenozoic rocks present total some 15,000 feet of sediments ranging from the Salina-Negritos formation of Lower Eocene age to the Cone Hill

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formation of the Upper Eocene Chira Group. Shales, sandstones, and conglomerates show lateral facies changes and, sometimes, as in the Talara Group, rhythmic alternation of sands and shales. The lithologies suggest conditions of

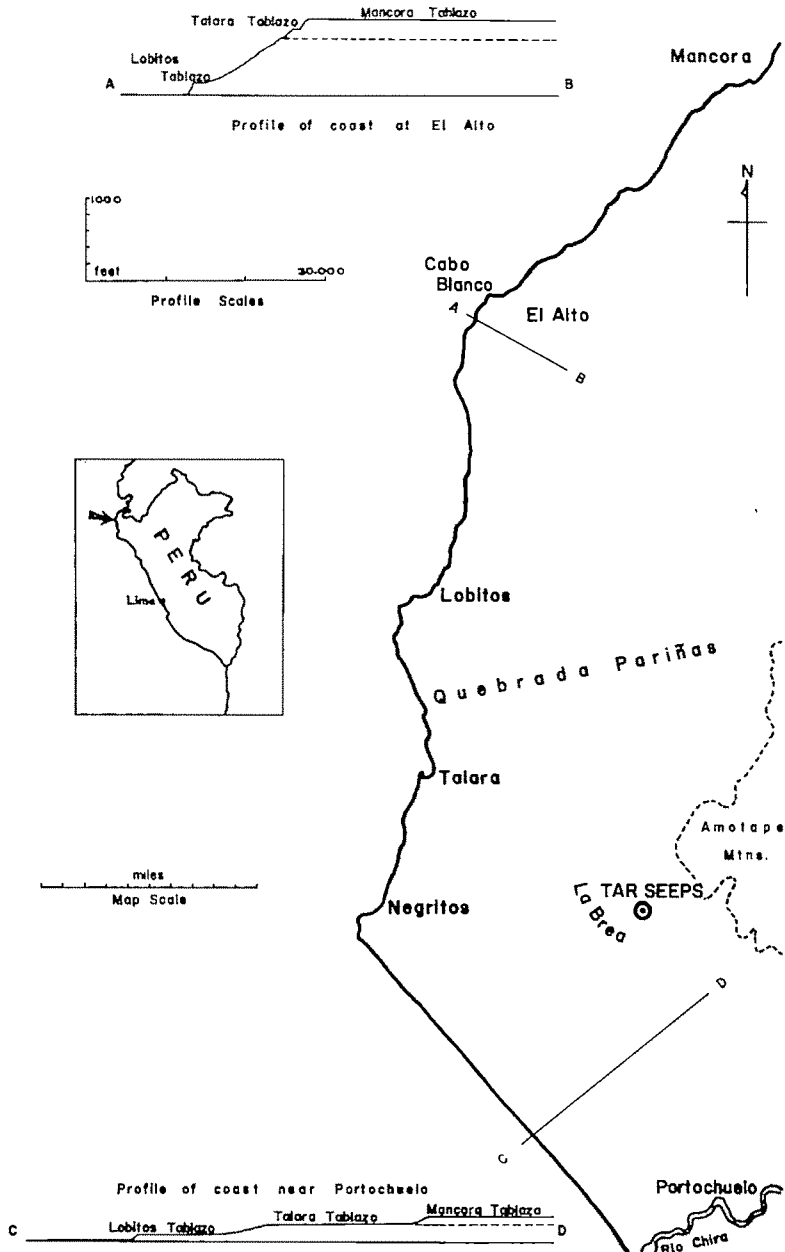


Fig. 1. Sketch map of Talara region, northwest Peru.

deposition ranging from a moderately deep water marine environment to shallow brackish water. Many of the sands, notably the Pariñas sand, are oil producers. The whole area is complexly block faulted.

Bosworth (1922) considers the geology and paleontology of the Cenozoic rocks, and a more recent summary of the pre-Pleistocene geology, with a comprehensive bibliography is given by Travis (1953).

PLEISTOCENE MARINE DEPOSITS.

Overlying a truncated surface of Cenozoic and older rocks is a thick sequence of marine quartz sands, shelly and calcareous sands, marls, coquinas, and pebble beds ranging in age from Early or Middle Pleistocene, to Late Pleistocene and Recent.

These deposits occur at three distinct levels, each one marking a period of marine encroachment followed by uplift of the coastline. These three levels or tablazo (tableland) surfaces are named from the highest and oldest to the lowest and youngest, respectively, Mancora, Talara, and Lobitos (Bosworth, 1922). The depression and uplift were not uniform along the coast, and all three surfaces attain their highest altitudes in the north and become progressively lower towards the south. Likewise the associated deposits are in each case thickest in the north.

At least three tablazo surfaces and associated deposits occur in southwestern Ecuador and have been briefly described by Sheppard (1937). In the Santa Elena peninsula, tablazos occur at 10, 250, and 350 feet above sealevel, whereas on the Isla de la Plata what are considered to be equivalent tablazo surfaces are found at 100, 500, and 740 feet above sealevel. The tablazo deposits are generally thin and said rarely to exceed 50 feet in thickness. The faunas appear to be similar to that of the Lobitos Tablazo and modern beach in northwestern Peru.

The Mancora Tablazo.—The Mancora Tablazo surface lies at about 900 feet above sealevel at El Alto in the northern part of the area and falls steadily to about 300 feet near the Chira River in the south, a distance of 45 miles. The Mancora Tablazo deposits reach a maximum thickness of 250 feet or more in the north and thin to less than 100 feet in the south. Some of the best exposures of the varied sands, coquinas, and pebble beds occur in the walls of the Quebrada Siches and other steep-sided valleys in the El Alto area.

Medium- to fine-grained, gray or yellowish or rusty-weathering quartz sands make up the greater part of the Mancora Tablazo deposits, particularly in the lower part of the succession. The sands are usually clean and well sorted and probably represent beach or offshore deposits laid down in water sufficiently shallow for effective winnowing by wave action, i.e., less than 30 feet (Bradley, 1958). They frequently show low-angle cross bedding and carry a scattered shelly fauna, *Ostrea megadon* Hanl. being particularly characteristic at some localities. In general the sands are only poorly consolidated, although iron-rich patches and bands are more resistant and tend to support the sands in vertical exposures. Individual sands vary from a few inches to 30 feet or more in thickness, and the thicker beds are persistent over many square miles.

The coquina bands within the succession occur mainly in the upper part and normally do not exceed 10 or 12 feet in thickness, although 25 feet has been recorded at some localities. They are more or less consolidated and relatively resistant to weathering so that they stand out as prominent ledge-forming horizons. In detail the coquinas are made up of comminuted shell debris cemented into a compact but usually quite open-textured or porous rock. Whole shells are common throughout and locally may be the dominant constituent. The barnacle *Balanus tintinnabulum* var. *concinus* (Darwin) often occurs in conspicuous masses. *Pecten purpuratus* Lamarck, *Ostrea megadon* Hanl., and a large species of *Ostrea* measuring up to 10 inches in diameter are also typically associated. *Turritella gonistoma* Val., *Thais chocolata* Ducl., and *Glycimeris ovata* Brod. are commonly found and locally may be the dominant forms. Rounded pebbles averaging $\frac{1}{2}$ to 2 inches in diameter and usually of brownish quartzite, graywacke, or pale gray or white quartz are usually present scattered throughout the coquina. Distinct pebble bands occur at some horizons and locally may form pebble beds up to several feet thick. Soft, fine-grained, gray to white marls are typically interbedded with the coquinas.

Along the face and top of the coastal cliffs between El Alto and the Quebrada Pariñas the coquinas take on a much harder and more compact character. The open saccharoidal texture typical elsewhere has been replaced by a dense texture in which the constituent comminuted shell debris is hardly discernible and where the large, intact shells present have been leached away, leaving only empty casts. The rock here is a true limestone, difficult to sample and breaking with a conchoidal fracture. This local modification of the coquina is presumably due to its exposed position on the cliffs. Although the prevailing southwesterly winds blowing off the cold Humboldt Current are practically devoid of moisture, the rapid ascent of the air over the cliffs, here over 800 feet above sealevel, does give rise to some localized condensation due to orographic effect. The moisture thus derived has been sufficient to cause solution and redistribution of the calcium carbonate in the coquina and leaching of the large shelly constituents. A similar phenomenon has been mentioned by Bosworth (1922) as occurring to the north in Ecuador where a moist climate prevails.

The abundance of unbroken and uneroded shells in the coquinas and the close association with calcareous sands and marls of extremely fine grain suggest deposition under quiet water conditions with little or no winnowing action. At some horizons, however, such features as cross bedding and pebble bands point to shallow water deposition with vigorous movement. The close association of these features would best be explained by postulating lagoonal conditions in this area in late Mancora time. There is today no direct evidence of a reef or barrier lying to the west, and protection for inshore water may have been provided, at least in part, by small reefs built up by lime-secreting colonial worms. Structures of this nature have been noted in the Mancora Tablazo deposits 8 miles east of Lobitos.

In the El Alto area the remains of numerous whales (Order Cetacea), mainly comprising vertebrae and fragments of ribs, have been found at several horizons in the upper part of the Mancora Tablazo succession. It has been sug-

gested (Cherry, 1953) that their presence supports the case, outlined in a later paragraph, for a whole series of raised beaches in the El Alto area, assuming that each whale marks the present position of the beach on which it was stranded. There is, however, no reason to suppose that such strandlines were any more than ephemeral features. Fluctuations in the profile of the beach and the building up of storm ridges in advance of a transgressing shoreline would, it is considered, be entirely efficient in burying and preserving intact some at least of such jetsam. The fact that some of the skeletons, particularly the vertebral columns, are almost undisturbed suggests that they were buried relatively rapidly. Alternatively they came to rest in quiet water, out of reach of vigorous wave action, possibly in shallow lagoons.

The spaces within the spongy bone structure have, in many cases, become more or less infilled by calcite, although there has apparently been little or no replacement of bone material. This has undoubtedly increased the resistance to weathering and presumably accounts for the prominence of many of the skeletal fragments on the surface at the present day.

The coquinas and interbedded sands and marls occur most prominently in the upper part of the Mancora Tablazo sections, particularly in the north of the region, while further south the deposits as a whole tend to be more sandy, a trend also seen in moving inland to the east. The overall north to south thinning of the Mancora deposits and the southward tilt of the Mancora surface would indicate greater crustal movements in the northern part of the region, both subsidence and subsequent uplift presumably being more pronounced than in the south.

In the north the Mancora Tablazo extends some 12 to 14 miles inland. With continuous and progressive marine transgression this could, according to the ideal wave-cut profile limitations of Bradley (1958), mean that the platform lay at about 1000 feet below sealevel in the El Alto area, assuming the simplest picture and leaving out of account any localized subsidence or tectonic warping. The Mancora succession in the area at the present time might, therefore, represent only one-third or less of the total thickness of sediments accumulated at the time of greatest advance of the Mancora sea, the younger deposits having been removed by subsequent erosion as the sealevel fell.

Differential weathering of the alternating coquinas and soft sands and marls is very marked and gives rise to the characteristic "stepped" topography of the El Alto area. Wind erosion is very effective in causing the wholesale removal of the sands and marls, whereas the thinner and impersistent coquinas are broken up by undercutting. Erosion of the thickest coquinas, on the other hand, is relatively slow, and their surfaces have become exposed over considerable areas. In some localities large fallen blocks help to protect the coquinas from undercutting and this must considerably slow down the retreat of the scarp edge. The great regularity and extent, often amounting to many square miles, of the more persistent coquina surfaces has led to the suggestion that they are in fact themselves raised beaches, marking intermediate sealevels below that which produced the main Mancora surface. Although lower beach levels probably did exist at intervals during the post-Mancora uplift, it is unlikely that their presence could be detected in erosion surfaces at the present

day. The difference in resistance between the coquinas and the sands is so marked and is so accentuated by the effects of wind erosion that the resultant topography completely masks any possible surfaces initiated originally by wave action alone.

The effects of wind erosion are also very noticeable on outcrops of Eocene rocks in the area where the varying resistance of alternating shales and thin-bedded siltstones and sandstones is reflected in a "stepped" topography in miniature.

With progressive uplift of the land the coquinas and sands not removed by erosion would have been covered by a veneer of prograded beach deposits (Bradley, 1957) laid down as the Mancora sea retreated. In view of the age of the Mancora surface the possibility of any of this veneer remaining seems small; nevertheless, intermittent but extensive patches of rounded pebbles occurring on the Mancora surface in the area north of the Quebrada Pariñas may, in fact, represent the deflated remnants of this final deposit of the Mancora sea.

The Talara Tablazo.—In the northern part of the area between the Quebrada Pariñas and El Alto only remnants of this tablazo surface and the associated sediments remain at the present day. In this region the Talara deposits were probably never of great east-west extent, and they now occur on narrow, disconnected ledges usually only a few hundred yards wide. At El Alto one such ledge, lying 95 feet below the Mancora surface, shows strongly cross-bedded coquinas dipping steeply towards the west and representing beach debris piled against an old sea cliff developed in deposits of Mancora age. At a locality 6 miles south of El Alto, exposures in a gulley section show cross-bedded sands deposited against an old cliff cut into Tertiary sandstones overlain by Mancora Tablazo sediments.

South of the Quebrada Pariñas the western edge of the Mancora surface swings inland in a great arc to the east and southeast, and the Talara surface occupies a large area within this shallow embayment, extending approximately 10 miles in an east-west direction at its widest. At Talara the surface lies at about 280 feet above sealevel, dropping gradually southwards to about 130 feet at the southernmost occurrences north of the Chira River. The Talara deposits are everywhere thin and even at their greatest development in the north seldom exceed 25 feet. In the Talara area 8 to 12 feet is the average and this thins to 5 feet or less in the south.

The deposits are predominantly pebbly in character and vary from pebble beds made up almost entirely of rounded graywacke, quartzite, or quartz pebbles with little or no shelly material, to pebbly and sandy coquinas interbedded with shelly marls. *Pecten purpuratus* Lamarck, *Ostrea megadon* Hanl., *Glycimeris ovata* Brod., *Arca grandis* Brod. and Sow., the large, thick-shelled species of *Ostrea*, *Turritella goniostoma* Val., and *Balanus tintinnabulum* var. *concinus* (Darwin) are all common forms found in the coquinas. In general the fauna is similar to that found in the Mancora Tablazo deposits although other species not noted in the older formation, such as *Chama pellucida* Brod., *Pecten tumbezensis* Orb., and *Anomia peruviana* Orb., are present.

The wave-cut platform beneath the Talara deposits in places reaches 8 to 10 miles inland and, as with the Mancora Tablazo, this implies erosion during a progressive advance of the sea. In the offshore zone there was presumably deposition in the wake of the zone of active erosion during the Talara transgression but, as that zone retreated westward again in the closing stages of the Talara cycle, the sediments would have been removed.

The Talara Tablazo deposits, although varying locally, show little or no regional facies change and, compared with the deposits of Mancora age, amount only to a thin veneer. It therefore seems likely that they represent only a single cycle of deposition and were laid down during progradation of the beach deposits on the retreat of the Talara sea. This final erosion and progradational deposition would mask the effects of any minor fluctuations in sealevel during the major Talara transgression.

East and southeast of Talara are several pebble ridges aligned in a north-west-southeast direction parallel to the Talara shoreline. Usually these are barely discernible as topographic features on the ground but can be readily seen on air photographs. They may represent storm beaches on the shore of the retreating Talara sea.

Lobitos Tablazo.—The Lobitos transgression was short lived with a wave-cut terrace probably never more than a mile wide. As with the Talara Tablazo the Lobitos deposits are of prograded beach type laid down as the sea withdrew.

Erosional remnants, often reduced to only a few square yards of flat surface, occur at intervals along the coast from Mancora to Talara. In the northernmost localities the surface lies at about 135 feet above sealevel, falling to 72 feet at Cabo Blanco and 67 feet at Lobitos. At Cabo Blanco the tablazo occurs beneath recent guano deposits up to 1 foot thick.

Southeast of Negritos the tablazo occurs as a narrow ridge running for about 7 miles parallel to the present shore; this represents the largest portion of Lobitos Tablazo surface remaining. At its southern end the ridge is $2\frac{1}{2}$ miles from the present sea margin and lies behind a broad stretch of sand dunes and salinas. The surface here is 50 feet above sealevel.

The Lobitos Tablazo deposits, like the Talara Tablazo, are largely pebbly in character. As in the older tablazos there is considerable local variation; in some areas sandy and pebbly coquinas are richly fossiliferous both in the number and variety of forms, while in others, particularly close to the old sea cliffs, coarse pebble beach deposits are practically barren of fossils. Thicknesses normally range from 4 to 10 or 12 feet with the thicker sections occurring in the more northerly localities.

The most marked features of the Lobitos fauna, when compared with the older assemblages, are the great increase in the number of gastropod species, the greater total number of molluscan species present, and the absence of such forms as *Pecten purpuratus* Lamarck and the large *Ostrea* sp. so characteristic in the Mancora and Talara Tablazo deposits. The fauna is similar to that found on the modern beaches and on the whole shows a warmer aspect than does the Mancora and Talara assemblage. As Bosworth (1922) has suggested, this change probably reflects variations in the configuration of the coastline. At the

present day the cool Humboldt current tends to be deflected by the westerly-jutting points of land such as Punta Balcones. In consequence the ameliorating influence of the southward-setting warm counter current (El Niño) is felt, although with decreasing effect, as far south as Paita. During Mancora and Talara times, on the other hand, the Humboldt Current apparently carried further north before being deflected westwards, and so along this portion of the coast the influence of the counter current was negligible.

Although along the Pacific coast of North America upwelling of coldwater has been suggested as a factor in determining the distribution of Pleistocene molluscan faunas (Valentine, 1955), there is, up to the present, no evidence for any such effects along the Peruvian coast.

RECENT SEDIMENTS

Salina deposits.—At the mouth of the Quebrada Pariñas and in the area south of Negritos are broad flats covered by blown sand, shells, and extensive salinas or salt flats liable to inundation at the highest tides. These are areas only recently emergent as a result of the latest phase of uplift of the coastline following the slight negative movement that caused the removal of much of the Lobitos Tablazo deposits and the erosion of the post-Lobitos cliffs.

Although apparently attributable to the same process of marine regression, the Salina deposits are markedly different from those of the Lobitos Tablazo. These differences might be explained by appeal to a rapid uplift, leaving no time for the inevitable progradation required by Bradley, but the answer possibly lies in the fact that neither the Quebrada Pariñas flats nor those south of Negritos are true emergent open beaches. Both are physiographically more in the nature of estuaries and are underlain by considerable thicknesses of alluvial sediments. In the case of the Negritos area the mouth of the river lies at the north end of the salina flats, and there are numerous records of the breaching of the coastal dunes during times of flood.

The situation is further complicated by the thick accumulations of blown sand. In the area south of Negritos, ridges of sand and shells reach over 30 feet in height. Their straight alignment parallel to the general trend of the coast suggests that they originated on a foundation of storm ridges on the early shelly and sandy beach left as the sea retreated.

Amotape Breccia Fan.—This is the name applied to the great fan of downwash material derived from the Amotape Mountains to the east. It blankets much of the Mancora Tablazo surface in the eastern part of the area and by successive reworking during intermittent floods has come to spread over considerable areas of the Talara surface also, reaching as a thin remnant almost to the present coast. Typically it consists of a coarse, angular gravel made up of reddish brown- and rusty-weathering graywacke and quartzite fragments. Around the flanks of the Amotape Mountains it is very coarse grained and irregularly and deeply eroded by channels gouged out in times of torrential rains. Further away from the mountains the deposit is of smaller grain size and somewhat better sorted, covering large areas as a flat stony desert pavement.

Blown sand.—Blown sand carried inland from the beaches by the prevailing southwesterly winds chokes many of the smaller valleys and accumulates

in every hollow and in the lee of all obstructions. The most extensive areas occur where there is a scattered vegetation cover and mounds of sand pile up in the lee of the thorn bushes. Only locally near the coast, as in the area south of Cabo Blanco and near Portochuelo, are true dunes with slip faces developed.

THE TALARA TAR SEEPS

Numerous surface tar seeps occur in the La Brea-Pariñas oil field area, the largest being in the region some 10 miles southeast of Talara. The seeps have been known since early times, and pitch was obtained there by the Indians and later by the Spaniards. Numerous pits, up to 20 feet deep, remains of the hearths and iron crucibles used for boiling off the light ends, and large numbers of earthenware shards are to be seen at the present time. It was at this locality that the first oil well in Peru was drilled in 1862.

The main seeps lie within the area of the concession or Estate of the International Petroleum Company, and the presence of bones in the brea deposits associated with the seeps had been noticed for some years. The first real attempt to collect the material, however, was made by G. H. McDonald and R. B. Fraleigh, geologists with the Company, and a representative collection was sent to the Royal Ontario Museum, Toronto in 1957.

The vicinity of the main tar seeps is known by the name La Brea (Spanish for pitch) and on the maps of the International Petroleum Company the productive area is known as the La Brea pool. In view of the possibility of confusion with the well-known Pleistocene vertebrate locality at Rancho La Brea, California (sometimes referred to only as "La Brea" in the literature), it is proposed henceforth to refer to the present locality as the Talara tar seeps.

The seeps occur upon the Mancora Tablazo surface and, as they lie only about 6 miles west of the Amotape Mountains, also in the area of the main Amotape Breccia Fan. The original surface of the seeps area has been partially destroyed by man-made excavations but enough remains to indicate that it stands at approximately the same level or a little above that of the general surface of the breccia fan, due to a gradual build up of pitch deposits assisted, in part at least, by the accretionary action of pitch exposed at fresh seeps which tends to trap blown sand and dust.

Sections exposed in man-made cuts show the tar seep deposits to consist of irregularly alternating lenses and stringers of medium to coarse, poorly sorted angular gravels and cross-bedded sands. Although, as will be seen later, there are numerous indications that permanent or semi-permanent streams were present in the area, the general aspect of the seep deposits is similar to that of the Amotape outwash sands and gravels of the present day desert surface and, in so far as their sedimentary structures are concerned, they cannot be said to provide positive evidence of deposition in a permanent stream. Detailed study of the size distribution of the gravels, shape of the pebbles, etc., may, however, show significant features not apparent in the field.

The main bone-bearing deposits occur as irregular lenses up to 6 feet thick and 20 to 30 feet in width. These may have been pools of pitch later filled with gravel and sand, or they may represent patches of tar-soaked quicksand into which the animals blundered. Most likely the seeps were covered by shal-

low pools of water or a stream which would, of course, provide a powerful attraction to animals.

At the present time small natural pools of pitch occur at the surface, but, unless the seep is persistently active, they are short lived and within a few days usually become sealed off as the pitch hardens, a process speeded by the smothering action of blown sand and dust.

Today large pools of pitch occur only in artificial hollows and trenches or adjacent to flowing wells. These are still active as traps of wildlife, and numerous birds, mainly water fowl, and large numbers of beetles, moths, and other insects were noted.

One of the outstanding features of the fossiliferous deposits is the great mixing and high percentage of broken bones. It is extremely improbable that any circulation of the tar could account for this; rather it is suggested that the bones became disturbed by the movement of later victims during their death struggles.

PLEISTOCENE CLIMATES

The vertebrate fauna found in the tar seep deposits includes many forms characteristic of a habitat considerably wetter than any found in the area at the present day. Although it is not possible to say with certainty that the whole region was well watered during Pleistocene times, there must have been numerous permanent or semi-permanent streams. This much can be adduced not only from the presence of the tar seep animals but also from the evidence of the deep river valleys cut into the elevated marine terraces and in the Amotape Mountains; their origin clearly dates back to a period of greater precipitation and runoff.

Further evidence is seen in the great abundance of vegetable material found throughout the fossiliferous brea deposits, including finely comminuted fragments of woody plants, twigs, thorns, seeds, and seed cases. A proportion of this material possibly represents debris washed in from higher ground upstream, and there is evidence also that some came from the stomachs of animals trapped in the seeps; nevertheless the abundance of the material is considered ecological evidence for at least a moderate vegetation cover in the immediate vicinity.

In the case of the invertebrate faunas of the tablazo deposits, a change towards warmer water conditions is suggested by the greater variety of forms in the Lobitos Tablazo deposits and on the modern beach as compared with the Mancora and Talara faunas. However, as was mentioned earlier, this probably reflects a change in the shape of the coastline and the consequent effect on the influence of the Humboldt Current rather than on a change from a colder climatic regime.

At the present day the aridity of the coastal plain is directly proportional to the intensity of the Humboldt Current influence and it is interesting to note that, unless regional climatic factors were of over-riding importance during Mancora and Talara times, the local climate might then have been even more arid than at present as a result of the more northerly sweep of cooler coastal water.

In South America, as in North America, there is evidence from many localities of an overall wetter climate during the Pleistocene (Charlesworth, 1957, p. 1122). Whether or not the Humboldt Current influence along the Peruvian coast was sufficient to maintain the arid state of the coastal plain it is difficult to say. It does seem likely that owing to the effect of the Humboldt Current the coastal plain climate was essentially arid but that the inland region, enjoying a wetter climate than at the present day, supplied a greater runoff to west-flowing streams and thereby enabled them to cross the coastal plain as permanent or semi-permanent rivers.

The presence of shell middens and ancient Indian occupation sites several miles from the coast in the Quebrada Pariñas and elsewhere in areas now completely devoid of any permanent fresh water suggests that even within a period of possibly only the last 1000 years there has been a continuation of the progressive desiccation of the region.

AGE RELATIONSHIPS

All the molluscs of the tablazo faunas so far identified appear to belong to species still extant. As mentioned in a previous section, the closely similar Mancora and Talara faunas differ somewhat from the Lobitos and modern assemblage, particularly in the lesser number of species present. The observed vertical intervals between the various erosion surfaces indicate that the Mancora/Talara and Lobitos/modern time intervals were relatively short, and that between the Talara and Lobitos phases was considerably longer.

The high shorelines of Pleistocene age recognized in many parts of the world as resulting from worldwide fluctuations in sealevel cannot, of course, be identified in the present series of tablazo surfaces. These owe their existence primarily to tectonic movements of the land and any effect attributable to sealevel fluctuations would have been completely masked.

Undoubtedly the most promising solution to the age problem lies in Carbon-14 analysis. Samples of shelly material from all three tablazo surfaces have been submitted for Carbon-14 analysis and it is hoped that direct dating of the tablazos will be possible. Radiocarbon dating of bone material from the tar seep deposits will also be attempted, although it is not certain how far it will be possible to eliminate the effects of the pitch with which all the bone deposits are saturated.

Relative to the tablazo surfaces a post-Mancora age for the main bone-bearing tar seep deposits is indicated by the presence, in close association with the bones, of scattered marine shells and shell fragments washed in from surface deposits of Mancora Tablazo material. At the other end of the scale it is fairly safe to assume that the main period of bone accumulation pre-dates the Lobitos Tablazo since the evidence of only a small uplift and the modern aspect of the Lobitos fauna points to a comparatively recent date for this phase.

The vertebrate fauna of the tar seeps suggests an Upper Pleistocene age. However, it is not possible to relate this assignment directly to the tablazo sequence and to say at what period within the relatively long Mancora-Lobitos interval the animals were trapped and buried.

GENERAL DESCRIPTION OF THE TAR PIT FAUNA

The collection of specimens from the Talara tar pits already shows one of the most complete faunal samples from the Upper Pleistocene of South America. This fauna will be referred to as the Talaran Fauna hereafter for brevity. The only comparable sample known at present is that from Rancho La Brea, California, and it is fortunate that two sites similar in age and formation are available for detailed faunal comparison.

The sample obtained includes remains of both plants and animals. The plant remains are divisible into two groups: large pieces of wood in varying degrees of preservation and obviously derived from fallen boughs of mature trees, and smaller pieces of wood only a few centimeters or less in length, seed pods, thorns, buds and soft ends of twigs, deposited while still green. These small pieces are from both woody and partially woody plants and probably originated in part from the remains of the stomach contents of the larger herbivores trapped in the deposits. The ends of the small twigs are often cleanly cut at an oblique angle, suggestive of the chopping action of the teeth of a sloth such as *Eremotherium*, or of the incisor teeth of some rodents. These small pieces are distributed throughout the matrix in an uneven manner, but mixing of the remains within the deposit has occurred and none of this material can be associated with the remains of any particular animal.

The animal remains include insects, molluscs, and vertebrates. The insect remains comprise scattered elytra, head and thoracic shields, mouth parts, and various parts of the abdominal segments and legs of various types of beetles. The genus *Hydrophilus*, family Hydrophilidae, has been tentatively identified, with at least ten other varieties of Coleoptera among the insect remains. Molluscan remains are represented by two shells of a small fresh water pulmonate, family Planorbidae, tentatively assigned to the genus *Gyraulus*.

The vertebrate remains include representatives of the classes Amphibia, Reptilia, Aves, and Mammalia. The amphibian remains consist of a few anuran femora and are scarce. The reptilian remains are referable to the Orders Crocodilia, Chelonina, and Lacertilia, and comprise fragments of jaws, long-bones, portions of carapaces, and bones from the skulls of crocodilians. The avian remains are mainly from the postcranial skeleton, but on the basis of both cranial and postcranial fragments identification of teal and duck (Anatidae, *Anas* ?), blackbirds (Icteridae, *Icterus* ?), finches (Fringillidae, *Paroaria* ?, *Spinus* ?), vultures (Cathartidae, *Vultur* ?, *Cathartes* ?), cormorants (*Phalacrocorax* ?), eagles and hawks (Accipitridae, *Aquila* ?), falcons (Falconidae), goat-suckers (Capromulgidae), and herons (Ardeidae) can be reported tentatively. The mammalian fauna is represented by parts of the skeletons of Marsupialia, Chiroptera, Edentata, Rodentia, Carnivora, Perisodactyla, Artiodactyla, and Proboscidea. The faunal sample is therefore fairly broad at the higher level, and although some obvious gaps are present (e.g. Squamata, Primates) at the time of writing, it is reasonable to expect further additions as new prepared material becomes available.

Owing presumably to the trampling and threshing of the larger animals trapped in the tar, a large proportion of the bones are broken and well mixed within the deposit, very few articulated bones or parts of skeletons having been

found. The possibility of obtaining single individuals from this deposit is therefore small, and the construction of any skeleton will necessitate the compounding of a number of bones from different individuals. Many of the bones show damage because of exposure and weathering before they were entirely included within the matrix. Tooth-marks of rodents and carnivores are also evident, and some show striae, possibly made by disarticulated bones rubbing against each other or against stones or teeth during the struggles of the trapped animals. A marked preponderance of phalanges, metapodials, and vertebrae of the other bones of the skeleton of the larger animals in the deposit suggests some selective agency at work. This may show a preference by carnivores for the meatier parts of the bodies and for marrowbones and a distaste for the extremities which would have been covered with pitch. The extremities would then be disregarded and become entombed in the pitch in an unbroken state, while the remainder of the skeleton would be broken for its contents or in the death struggles of the dying victims.

The tar has stained all the bones and plant remains black, often filling the alveoli, sutures, and sinuses with a hardened pitch deposit. Where weathering has occurred, the color may be bleached to a dark brown, and in this latter condition the bones are often brittle and friable.

FAUNAL RELATIONS

Climatic evidence.—The topography of Ecuador and Peru is divisible into three main sections, a western low-lying Pacific littoral region, a central high Andean region, and an eastern low-lying Amazonian basin region. These three regions possess different climatic environments despite their tropical latitudes, the climatic variation being dependent upon differences in altitude and rainfall peculiar to each region. The present-day faunas of these regions are highly diverse and reflect respectively a dry semi-desert along the Pacific coast, a montane environment in the Andes, and a tropical rain forest in the low Amazon basin. The Talaran fossil fauna is from an environment which is dry semi-desert today, and the extant fauna has few species in common with the Andean or Amazonian faunas. It can be reasoned that the Talaran fossil fauna should include few representatives from the other two life zones. This is borne out by the obvious tropical character of the Talaran assemblage which shows little affinity with the faunas of the tropical rainforest. Instead it suggests a relatively open grassland interspersed with some trees, such as occurs in the savannas and bushveld of southern Brazil or Africa at the present day. This type of environment is wetter than that of the Talara region today, and the presence of bones of Crocodilia and Anura, remains of Hydrophilidae, Anatidae, Phalacrocoracidae, and Ardeidae, and the presence of fragments of wood from large trees that may have been nearby all support this contention. Perhaps the climate was one in which seasonal rains and partial droughts occurred cyclicly, the faunal population migrating into the area during the wet seasons.

Probably the Talara tar pits attracted and held individuals representative of the local fauna in the same manner as did the tar pits of Rancho La Brea in California. Herbivores would have been attracted by water, some of it standing over the impermeable surface of the tar pools, and would have become

trapped in the soft tar when they attempted to wade into the water. Carnivores would have gathered around the trapped herbivores to feed upon the dead and dying, and in their turn would have become trapped. Others might have been trapped in attempting to cross areas of viscous tar covered by a layer of wind-blown sand.

The presence of mastodonts (*Haplomastodon*) indicates that at times the hard crust on the surface of the tar pools must have been almost strong enough to support the great weight of the animal, since the caution of the living proboscideans and their habit of testing the ground before venturing to place their whole weight upon a foot is well known. During the dry weather their natural caution would be blunted by the need for water, and the animal would venture upon the crust overlying the tar pool. Such a crust might form during a prolonged drought, being made up of tar-soaked sands or of laminations of pitch and windblown sand baked hard by the sun.

The presence of various other creatures usually found associated with water supports the theory that standing water was the main attraction. Remains of crocodilians and of wading and swimming birds have been mentioned already. The crocodilians (and anurans) could have come from the nearby coastal areas or river systems during periods of heavy rains, when they are known to wander away from water, and the aquatic birds could have seen the water from the air, and tried to land upon it. In both cases, if the water coverage was only a few inches deep and the tar still soft beneath it, the force of the creatures entering the water would have been sufficient to trap as heavy a creature as a crocodilian and to have congealed the feathers of a bird so that it could not escape. Alternatively, the crocodilians may have been attracted by the carcasses present, and been trapped in the same manner as were the other carnivores. Birds and water beetles might have mistaken the shining surface of fresh tar for pools of water, as, in fact, they do today.

Geographic evidence.—A marked correspondence between the faunas of the Carolinian of Ecuador and the tar pits of Talara is seen when a comparison is made of the mammalian genera tentatively identified from Talara with those reported from Rancho La Brea (Stock, 1958), and from the Pleistocene of Ecuador by Hoffstetter (1952). The Carolinian fauna of Ecuador is from the coastal region between Guayaquil and Portoviejo, and is Upper Pleistocene in age. Ten genera certainly and possibly two other genera are common to both the Carolinian and Talaran deposits, and four to Rancho La Brea and Talara.

Table 1 shows a comparison by genus and subgenus of the main elements of the mammalian faunas of the tar pits of Rancho La Brea and Talara, and with the three main groupings of the Ecuadorian faunas (Hoffstetter, 1952). The nomenclature used follows Simpson (1945). A difference between the Talaran and Carolinian faunas is the absence of megalonychid remains from Talara.

The presence of marsupials in the fauna is indicated by a fragment of a left mandible with seven alveoli (approximate length 7 mm), and while it shows various didelphid characters, it is lacking teeth, symphyseal, and articular areas, and therefore detailed comparison is impossible. The closest comparison is with the modern genus *Marmosa*; tentatively it may be considered

TABLE 1

Comparison of the fossil mammal faunas of Rancho La Brea, California (Stock, 1958), and Talara, Peru, and three faunas from the Pacific Coast, the Andes and the Amazon basin of Ecuador (Hoffstetter, 1952). 'X?' = tentative generic identification. The following orders and families have been omitted from this table as they appear only in the Rancho La Brea fauna: Insectivora, Lagomorpha, Ursidae, Bovidae, and Antilocapridae.

Order: Family Genus or Subgenus	Rancho La Brea, Cali- fornia, North America, U. Pleistocene	The Talara tar seeps, Peru, South America	Carolinian, Pacific Coast of Ecuador, U. Pleistocene	Punian and Chichean, Ecuador, U. Pleistocene	Amazonian of Ecuador, ? Pleistocene
MARSUPIALIA					
<i>Didelphidae</i>			Gen. indet.		
<i>Marmosa</i>		X?			
CHIROPTERA					
<i>Microchiroptera</i>					
<i>Eptesicus</i>		X?			
EDENTATA					
<i>Megalonichidae</i>			Gen. indet.		
<i>Nothrotherium</i>	X				
<i>Megalonyx</i>	X				
<i>Mylodontidae</i>					
<i>Paramylodon</i>	X				
<i>Glossotherium</i>		X	X		
<i>Scelidotherium</i>		X	X		
<i>Oreomyodon</i>				X	
<i>Megatheriidae</i>					
<i>Eremotherium</i>		X	X	X	X
<i>Dasypodidae</i>					
<i>Chlamytherium</i>		X	X		
<i>Propaopos</i>				X	
RODENTIA					
<i>Hydrochoeridae</i>					
<i>Nechoerus</i>		X?	X		
<i>Capromyidae</i>					
<i>Drytomomys</i>				X	
<i>Echimyidae</i>					
<i>Proechimys</i>			X		
<i>Sciuridae</i>					
<i>Otospermophilus</i>	X				
<i>Geomyidae</i>					
<i>Thomomys</i>	X				
<i>Heteromyidae</i>					
<i>Perognathus</i>	X				
<i>Dipodomys</i>	X				
<i>Cricetidae</i>					
<i>Reithrodontomys</i>	X				
<i>Peromyscus</i>	X				
<i>Onychomys</i>	X				
<i>Phyllotis</i>		X?			
<i>Sigmodon</i>		X?			
<i>Neotoma</i>	X				
<i>Microtus</i>	X				

TABLE 1 (Continued)

Order: Family Genus or Subgenus	Rancho La Brea, Cali- fornia, North America, U. Pleistocene	The Talara tar seeps, Peru, South America	Carolinian, Pacific Coast of Ecuador, U. Pleistocene	Punian and Chiclean, Ecuador, U. Pleistocene	Amazonian of Ecuador, ? Pleistocene
CARNIVORA					
<i>Canidae</i>					
<i>Canis</i>	X				
<i>Aenocyon</i>	X	X			
<i>Urocyon</i>	X				
<i>Dusicyon</i>		X	X	X	
<i>Protocyon</i>			X		
<i>Felidae</i>					
<i>Panthera</i>	X	X		X	
<i>Puma</i>	X		X	X	
<i>Smilodon</i>	X	X	X	X	
<i>Lynx</i>	X				
<i>Mustelidae</i>		Gen. indet.			
<i>Mustela</i>	X				
<i>Mephitis</i>	X				
<i>Spilogale</i>	X				
<i>Taxidea</i>	X				
PROBOSCHEA					
<i>Gomphotheriidae</i>			Gen. indet.	Gen. indet.	Gen. indet.
<i>Haplomastodon</i>		X	X	X	
<i>Cuvieronius</i>				X	
<i>Mammuthidae</i>					
<i>Mammuth</i>	X				
<i>Elephantidae</i>					
<i>Elephas</i>	X				
PERISSODACTYLA					
<i>Equidae</i>					
<i>Equus</i>	X				
<i>Amerhippus</i>		X	X	X	
<i>Onohippidium</i>				X	
<i>Tapiridae</i>					
<i>Tapirus</i>	X?	X?			
ARTIODACTYLA					
<i>Camelidae</i>					
<i>Camelops</i>	X				
<i>Tanapolama</i>	X				
<i>Palaeolama</i>		X	X	X	
<i>Cervidae</i>					
<i>Odocoileus</i>	X	X	X	X	
<i>Mazama</i>				X	
<i>Agalmaceros</i>				X	
<i>Tayassuidae</i>					
<i>Platygonus</i>	X				

to belong to this genus. The Order Chiroptera is represented by a number of mandibles and isolated teeth. Comparison of the mandibles and of the teeth with specimens of *Eptesicus* shows marked similarities, and provisionally the Talaran form is assigned to that genus.

The presence of a hydrochoerid rodent of the genus *Nechoerus* is attested by some phalanges. These have been tentatively assigned to *Nechoerus*, as *Nechoerus* has been reported by Hoffstetter; alternatively the genus may be *Hydrochoerus*.

The cricetid rodent remains represent a large animal, similar to *Sigmodon*, but represented only by scarce and worn material, and two smaller forms, similar to *Phyllotis*, which are more abundantly represented.

Carnivores present in both the Carolinian and Talaran are *Dusicyon* and *Smilodon*. Two carnivore genera present in the Carolinian and absent in the Talaran are *Puma*, (*Felis* (*Puma*)), and *Protocyon*. These large carnivores are replaced by *Panthera* and *Aenocyon*, a South American giant jaguar or lion and a dire wolf closely related to, if not identical with, the Californian giant jaguar and dire wolf from Rancho La Brea (Churcher, 1959). *Panthera* will be used for the form similar to *Felis atrox* as Merriam and Stock (1932) refer to this cat as *Felis* (*Panthera*) *atrox*, and Simpson (1945) raises *Panthera* to generic rank. The presence of *Aenocyon* in Peru extends its range into South America, the most southerly previous record being from Tequixquiac, north of Mexico City (Furlong, 1925), other records for South America being doubtful.

The mustelid remains comprise two mandibles, three separate teeth, and a left humerus. The dentitions are worn and further material will be required for accurate identification, but the humerus is short and heavy and resembles that of *Mephitis*, the North American skunk. The animal is therefore probably one of the genera of South American skunks. The tapirid remains comprise only a few phalanges. As in the case of Rancho La Brea (Stock, 1958), these phalanges resemble most closely those of a tapir when compared with material or illustrations, and are provisionally identified as *Tapirus*.

Temporal evidence.—The age of the Carolinian is given as Upper Pleistocene by Hoffstetter. In terms of the Tablazo succession, the age of the Talaran tar-seep fauna is post-Mancora, possibly post-Talara, and probably pre-Lobitos, and probably within the upper half of the Pleistocene. A comparison of the two faunas shows that they are nearly identical in both ecology and composition, and from this may be deduced a close temporal relationship within the Upper Pleistocene.

The two main differences in the fauna, apart from deficiencies within the samples, are the substitution of *Protocyon* in the Carolinian by *Aenocyon* in the Talaran, and the substitution of *Felis* (*Puma*) *platensis* by *Panthera atrox*. The Pacific coastal zone is isolated from the rest of South America by the Andes, which provide a barrier to any migration of fauna from the eastern pampas of the Argentine and Brazil. Both *Protocyon* and *Felis platensis* were originally described from the eastern pampas and later identified from areas west of the Andes. *Aenocyon* and *Panthera atrox* were originally described from North America and are best known from the tar pits of Rancho La Brea. Both *Aenocyon* and *P. atrox* are larger and more massive carnivores than the South American *Protocyon* and *F. platensis* and were better adapted to prey upon the large herbivores. The explanation may be that the two larger forms

entered South America by the isthmus of Panama and migrated down the Pacific coastal plain towards Talara. The immigration of these two forms displaced the other two carnivores from the region west of the Andes, but representatives of *Procyon* and *F. platensis* survived east of the mountains. If this interpretation is correct, then the Talaran is later in time than the Carolinian of Ecuador.

There is another possible explanation which would, however, shed very little light on the temporal relationships of the two faunas. Since both *Aenocyon* and *P. atrox* are stronger and larger than *Procyon* and *F. platensis*, it is possible that in the region of the tar pits, where meat was reasonably easy to obtain, the two pairs of carnivores competed for the carcasses. Under these conditions the stronger *Aenocyon* and *P. atrox* might be able to drive away the weaker *Procyon* and *F. platensis*, and so have the privilege of feeding on the carcasses and becoming victims of the tar pits. This would account for the preservation of many specimens of *Aenocyon* which seems to have been primarily a scavenger. The many remains of *Smilodon* would also be accounted for, as this cat probably preyed on the large and slow herbivores, and would be attracted to the tar seep in the hope of easy prey. *P. atrox* is much scarcer, as at Rancho La Brea, and probably was a "lion" of the savannas accustomed to killing its prey by the same means as do the modern lions; consequently it would be less attracted by the trapped animals, and the number of specimens preserved would not be indicative of the total in the same way as are those of *Smilodon* or *Aenocyon*. At the time of writing, numerous bones of *Aenocyon*, *Smilodon*, and some of *P. atrox* have been recovered, while the field fox, *Dusicyon*, is represented by bones from all parts of the skeleton found throughout the deposits. On the other hand, no specimens of *Procyon* and *F. platensis* have yet been found and it seems improbable that either was present in the region of the tar seeps during the main period of trapping. Therefore, the explanation of the differences between the two faunas as involving an ecological separation may be discarded as unlikely.

The remaining possibility is that *Aenocyon* and *P. atrox* were originally present in the area and later were replaced by *Procyon* and *F. platensis*. This is also unlikely since *Procyon* is generally considered to be more primitive than *Aenocyon*, whereas *Panthera atrox*, one of the largest of the cats, is much larger than *F. platensis*. For *F. platensis* to replace *P. atrox* conditions would have had to favor the smaller form. No evidence of this can be adduced, as large herbivores of all sorts were still present, providing sufficient meat for the largest of the felids.

The presence of *Panthera (Jaguaris)* in the Punian and Talaran, and the absence of *Aenocyon* from the Punian suggests that the age of the Punian lies between the ages of the Carolinian and the Talaran. The sequence from older to younger would therefore be Carolinian-Punian-Talaran. To attempt to place the Chiclean and other Pleistocene horizons of Hoffstetter within this series would be incautious; too little is known of their faunas to provide evidence of their temporal relations. However, it is probable that they are all Upper Pleistocene in age and that their faunal differences represent ecological variation as much as temporal differences.

SUMMARY AND CONCLUSIONS

Successive uplifts of the coastal region of northwest Peru, with intervening periods of stillstand and negative movement occurred during the Pleistocene period. Three major erosion surfaces, the Mancora, Talara, and Lobitos Tablazos, and associated deposits are recognized. These surfaces are highest in the northern part of the area (approximately 900, 800, and 70 feet above sealevel at Cabo Blanco respectively). Traced southwards the tablazos become progressively lower and there is a corresponding decrease in thickness of the sediments.

The Mancora Tablazo deposits, up to 250 feet thick, are dominantly sandy in their lower part but with prominent coquinas and shelly marls, particularly in the north, in the upper third of the succession. The sediments are mainly of shallow water type and are considered to have been laid down as nearshore, and possibly in part lagoonal, deposits. The Talara and Lobitos Tablazo deposits, mainly pebbly sands and marls, are much thinner and are thought to represent prograded beach deposits laid down on the retreat of the Talara and Lobitos seas respectively.

All three tablazo deposits contain a prolific molluscan fauna, all specimens identified to date belonging to modern species. The Mancora and Talara faunas are closely similar and reflect a cooler water environment. The Lobitos fauna, similar to that of the modern beach, is of warmer water type and is characterized by a greater variety of species and a higher proportion of gastropods. These faunal differences suggest that the ameliorating effect of the southward-setting warmer counter current felt at the present day and in Lobitos time, was less pronounced in Mancora and Talara time.

The climate of the coastal region during Pleistocene time may have been as arid as at present. However, there were probably numerous permanent or semi-permanent streams crossing the coastal tract and fed by runoff from the mountains to the east where it is likely that a climatic regime appreciably wetter than at the present day prevailed.

Actual ages for the Tablazos have not yet been established and await the result of Carbon-14 analyses. A consideration of the relative heights of the three tablazo surfaces, supported by faunal evidence, suggests that the interval between the Mancora and Talara phases of deposition was comparatively short. This was followed by a long Talara/Lobitos interval, followed in turn by the relatively brief Lobitos/Recent period.

Tar seeps occurring in the area 10 miles southeast of Talara were active during Pleistocene time and successful in trapping a varied fauna, mainly of vertebrates. The main period of bone deposition postdates the Mancora Tablazo but is probably older than the Lobitos phase of marine deposition.

A preliminary consideration of the faunas of the Talara tar pits and the Carolinian of Ecuador shows that the Talaran deposits are probably younger than those of the Carolinian. Both possibilities of equal age and of the Talaran's being older than the Carolinian are insupportable on the evidence of the associated faunas. Both the Talaran and Carolinian faunas are of Upper Pleistocene age and must have been closely spaced within the Upper Pleistocene.

In other respects the Talaran fauna resembles that of the Carolinian so closely that the two may be treated as one when considering the general relationships of the Upper Pleistocene of the coastal regions of Peru and Ecuador. These seem to lie mainly with the faunas of Eastern and Southern Brazil, as many genera are common to both regions. *Eremotherium*, *Scelidotherium*, *Chlamytherium*, *Smilodon*, *Amerhippus*, and *Palaeolama* are present in both regions, and while differences at the specific level or less are to be expected, and have been reported by Hoffstetter for the Carolinian, the evidence points to the presence of a fairly uniform aspect to the South American Pleistocene fauna of the tree savannas. A few North American genera are found in later deposits representing this fauna, of which *Aenocyon*, *Panthera*, *Odocoileus*, and *Cuvieronius* are examples.

ACKNOWLEDGMENTS

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THE KAALIJARV METEORITE CRATERS ON SAAREMA ISLAND, ESTONIAN SSR*

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ABSTRACT. A group of one large and six small meteoritic craters in Estonia has been investigated in some detail, both morphologically and as to content of meteoritic fragments. Arguments are presented for considering the large crater an explosion crater arising from the collision of a large meteorite at remaining cosmic velocity. The explosion destroyed the meteorite and blasted the crater in the ground. The small craters, on the other hand, although arising from members of the same meteorite shower, are impact craters. The smaller fragments responsible for impact craters had been slowed down by atmospheric drag to the extent that they had no remaining cosmic velocity on impact, and no explosion occurred. Unlike the large crater, the small craters do contain fragments of meteorites.

The Estonian craters are compared with similar groups elsewhere, notably Sikhote-Alin, U.S.S.R.; Henbury, Australia; and Brenham, Kansas. (D. Hoffleit)

INTRODUCTION

The remarkable group of craters known as KaaliJarv meteorite craters (fig. 1) are located 20 km to the northeast of the town of Kingisepp (formerly Kuressaare) on Saarema Island, in the Estonian Soviet Socialist Republic (Krinov, 1955). The craters aroused the interest of scientists as far back as the first quarter of the last century. Since then researchers have repeatedly attempted to establish the nature of the craters and explain the conditions of their formation. In 1927, I. A. Reinwald, a mining engineer, began a study proving that they were of meteoritic origin.

The group consists of seven craters located in plowland covering an area of approximately 0.75 sq km (fig. 2). Seen from above, the largest has a regular round outline (fig. 3). It is 110 m in diameter and its rim rises 6 to 7 meters above the level of the surrounding terrain. The crater is filled with water and forms a picturesque pond about 16 m deep. Hence the bottom of the crater is 9 to 10 meters below the outer surface. On and around the rim of the crater there are large trees and bushes, making this unique parklike area easily seen from a distance, like an oasis in a desert. As distinct from the main crater, the other six remain dry and are of the following dimensions:

Crater No.	Diameter	Depth
	m	m
1	35	4.0
2	35 x 53	3.5
3	32 x 33	3.5
4	20	3.5
5	12 x 15	0.9
6	25 x 26	0.65

For hundreds of years local inhabitants have collected the stones from the fields they tilled here and thrown them into the craters. As a result the craters became filled with stones. Like the main crater, the smaller ones are overgrown with nut trees and can easily be seen from a distance. The stones and bushes have protected the craters against various agents of eolation.

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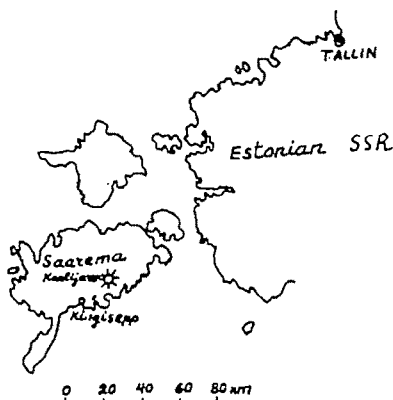


Fig. 1. Map of a section of the Estonian SSR and Saaremaa Island showing location of craters.

RECENT INVESTIGATIONS

On instructions from the Committee on Meteorites of the USSR Academy of Sciences, in the summer of 1959, L. G. Kvasha, a petrographer, I. T. Zotkin, an astronomer, and the author, accompanied by A. O. Aaloe, an Estonian geologist, investigated the craters.

The summer was dry and the water level in the main crater was considerably lower than usual, filling only the central part or very bottom of the crater. This made the crater's bowl-like shape, one of its chief peculiarities, clearly visible. The ramped layers of dolomite that rise at an angle of approximately 60° and protrude from the surface of the crater's rim (fig. 4) are especially impressive. In this area the dolomite bed, which is local sedimentary rock and consists of carbonate of lime and magnesite, is horizontal. It should be noted, as the second main peculiarity of the crater, that in all directions the elevation of the dolomite beds is radially outward from the center of the crater. Lastly, the third peculiarity is the clearly defined swell along the crater rim that rises steeply above the surrounding area.

The main peculiarity of the small craters is the presence of minute iron meteorite particles or meteoritic dust. One need only pull a magnet through the soil to collect particles of meteoritic dust; sometimes even small fragments of iron meteorites are found. In the main crater, on the other hand, despite repeated attempts no meteoritic dust has as yet been found.

Another peculiarity of the small craters is the complete absence of a swell and the elevation of the dolomite beds. Reinwald established (1928, 1939) that beneath elevated dolomite beds on the inside slope of the swell of the main crater there is a belt of dolomite which was crushed to a fine powder. In this "rock flour", lumps of soft dolomite were discovered that had been subjected to the influence of a high temperature.

In one of the small craters (No. 4), after partially excavating the matter with which it was filled, Reinwald discovered a depression about 0.5 m in diameter in the dolomite. The depression was in the lowest platform of the step-like bottom of the crater.

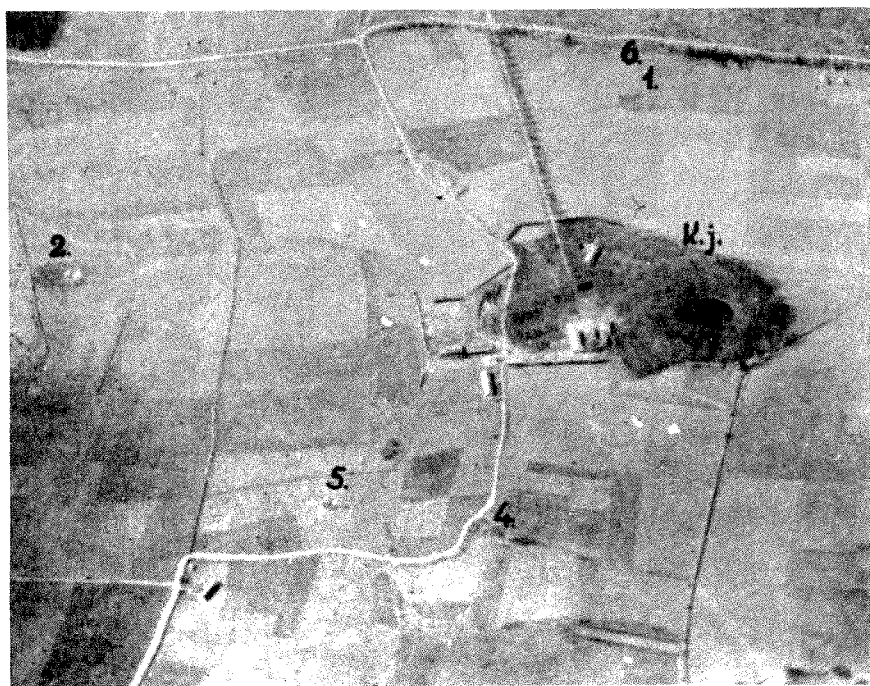


Fig. 2. Aerophoto of Kaalijary craters. Numbered according to I. A. Reinwald.

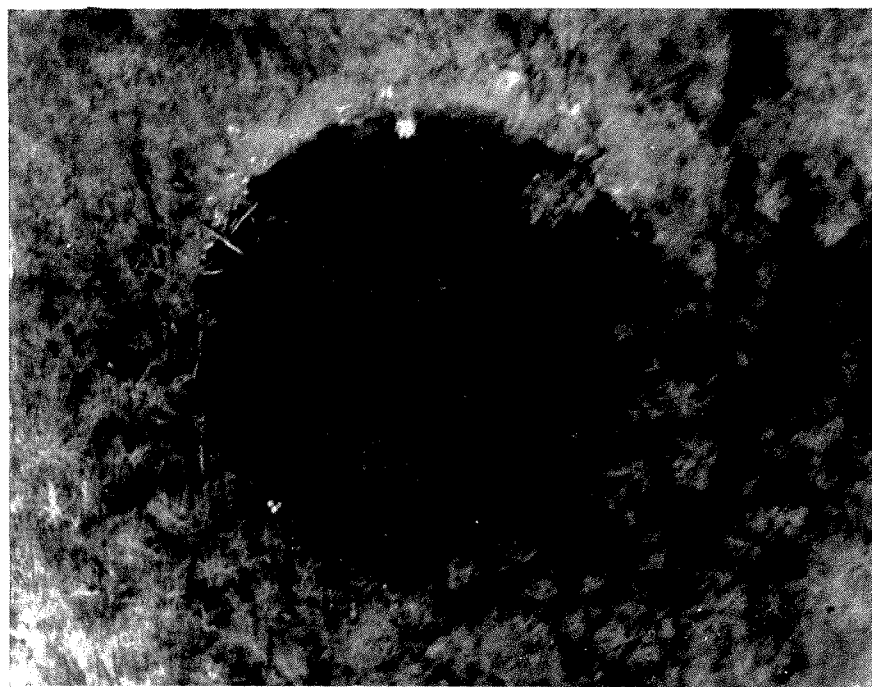


Fig. 3. Aerophoto of Kaalijary main crater (by I. A. Reinwald).

In 1929 the diamond drilling Reinwald undertook in the main crater showed that the dolomite had been entirely or partially crushed and burnt to a depth of 4 to 5 meters. Below this level the rock was normal. Reinwald again investigated the craters in 1937, partially excavating craters Nos. 2 and 5. Excavation in crater No. 2 to a depth of 2 m showed first a layer of soft soil 10 to 15 cm thick. Beneath this there was a compact brownish mixture consisting chiefly of small pieces of dolomite, rock flour, and clay-sand glacial deposits. The entire matter filling the crater had not been disturbed since the formation of the crater. In the filling matter at a depth of one meter, the first iron meteorite fragment was discovered: it weighed 24 grams and was covered with a thick layer of rust. On deeper excavation such fragments continued to be found. In the 80 cubic meters of matter removed during partial excavation, 28 meteorite fragments were found with a total weight of 102.4 grams; the weight of the individual fragments ranged from 0.1 to 24 grams.

In the other partially excavated crater (No. 5) two meteorite fragments weighing 4.8 and 3.4 grams were discovered, also covered by a thick layer of rust. In 1938 when Reinwald again excavated this crater he found another fragment which weighed 9.1 grams.

Chemical analysis of the meteorite fragments collected showed a nickel content of 8.3 percent. This amount of nickel is typical of the most common type of iron meteorites, medium structure octahedrites. Etching of the polished surface of one of the larger fragments revealed the typical Widmanstätten figures of this type of octahedrite.

By discovering meteorite fragments in the craters, Reinwald definitely proved their meteoritic origin. Unfortunately, he died in 1941 without having completed his study of the Kaaliyarv craters. At present the study of the craters is being continued by A. O. Aaloe, under the guidance of Academician K. K. Orviku of the Estonian Academy of Sciences. In 1955 Aaloe (1958) undertook partial excavation of crater No. 5, and found that the crater was formed in a stratum of basic moraine (no less than 1.2 m thick) and in layers of dolomite beneath it. In the northern part of the crater the surface of the original rock beds at a depth of 1.2 m forms steps along the inner slope of the crater (fig. 5). These steps were formed by the mechanical crushing of the dolomite by the fall of the meteorite. The bottom of the crater is in the original rock which is dolomite. Three meters from the western rim of the crater, a craterlike hole 22 cm deep and 60 cm in diameter was discovered in the meridional direction and 52 cm in the latitudinal direction. A study of this depression led Aaloe to conclude that it had been formed by the impact of a meteorite. Similar depressions, as mentioned above, were discovered by Reinwald also in crater No. 4; he, too, explained them as being due to the mechanical impact of a meteorite.

By means of a magnet, Aaloe collected 450 grams of iron meteoritic fragments, each over 1 mm in diameter, in the matter filling crater No. 5. He also collected meteoritic dust. Most of the fragments are less than 5 mm in diameter. Only 51 of them weigh over one gram each and six fragments weigh over 5 grams; the largest fragment weighed 8.62 grams. The fragments are of irregular shape and frequently have sharp edges. They are highly weathered, crusted with rust, often pierced by cracks, and break easily. Aaloe was the

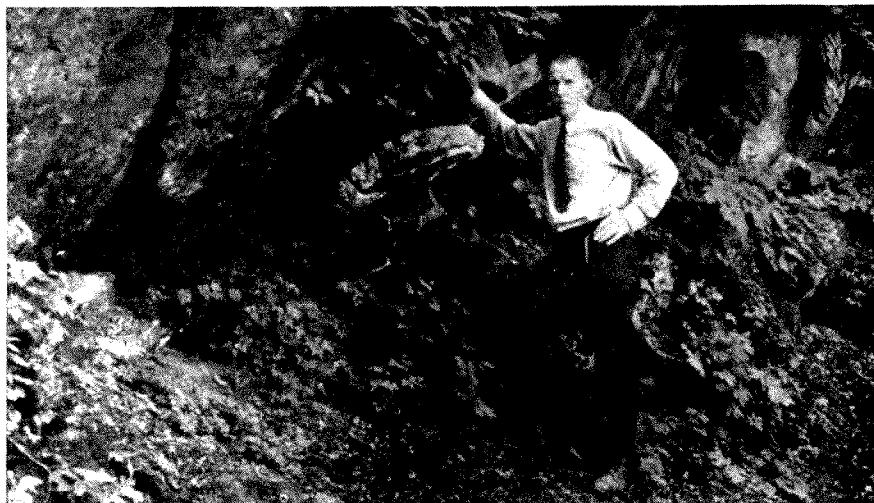


Fig. 4. Elevated dolomite layers protruding from the inside slope of the swell of the main Kaalijarvi crater. I. A. Reinwald is seen standing near the swell (I. A. Reinwald's photo).



Fig. 5. Step-like slope of the smallest crater, No. 5, after excavation of filling material. The horizontal layers of dolomite, chipped by the impact of the meteorite, can be seen. Standing inside the crater are (left to right): I. T. Zotkin, A. O. Aaloe, and L. G. Kvasha (Photo by E. L. Krinov).

first to discover magnetite globules from 0.15 to 6.4 mm in diameter. He believes that some of these globules may be particles of the dust train of the meteorite, i.e. meteoritic dust.

Lastly, among the matter found there were many broken and whole mollusc shells which, according to Aaloe and L. Sarva, a paleontologist, are typical of this damp coastal area. On this basis, they concluded that the formation of the Kaalijarv group of craters took place soon after the retreat of the littoral sea in the vicinity of Kaali, approximately 4000 to 5000 years ago.

At the time of the excavation of crater No. 5, E. Pobul took magnetometric measurements on crater No. 3. The measurements with two variometers were carried out according to a 1 x 1-m measuring grid. The measurements within the crater revealed weak and very local isometric micro-anomalies that are elongated in some places. On the basis of the magnetic measurements Pobul concluded that there are no large masses of meteoritic iron and that the magnetic anomalies he had discovered were due to very small agitators at a small depth. From experiments on the magnetic influence of the meteorite fragments collected in crater No. 5, Pobul concluded that small meteoritic fragments weighing no less than 20 grams can cause the magnetic anomalies that he discovered in crater No. 3.

It should be pointed out that in the main crater no meteorite fragments, meteorite dust or impactites—pieces of fused rock—typical of meteorite explosion craters have thus far been discovered.

A study of the fall of many meteorites (Krinov, 1955), including the remarkable Sikhote-Alin iron meteorite shower that fell in the Far East on February 12, 1947 (Krinov, 1956a, 1956b, 1959), shows that when meteoritic bodies move through the Earth's atmosphere at cosmic speed, they break up, as a rule, regardless of their composition or size (Krinov, 1958). Their breakup is caused by the extremely great atmospheric pressure on the front surface caused by their great speed, which exceeds 11 km per sec. At an altitude of 15 km above the Earth's surface this pressure reaches 100 kg per sq cm. The irregular polyhedral shape of meteoritic bodies to a considerable degree also promotes their breakup, causing uneven distribution of pressure on the surface of the meteoritic body and a steady, sometimes significant change in the atmospheric influence during the tumbling of the meteoritic body. The breakup of meteoritic bodies results in meteorite showers after which dozens, hundreds, and even thousands of individual samples may be collected. Meteorites from showers spread over an elliptical area called a dispersion ellipse. The individual samples from meteorite showers usually spread in the dispersion ellipse according to a definite order. The larger samples fall at the head or front of the ellipse, relative to the direction of motion, while the smallest samples fall in the opposite part or rear section, while samples of intermediate size fall in the middle of the ellipse.

It has, on the other hand, been established that atmospheric drag causes the meteoritic body or its remaining fragments to lose practically their entire cosmic speed at an average altitude of about 12 km. This section of the atmospheric path is called the region of delay. After passing through it, the fragments fall to the surface of the Earth like ordinary stones that have been



Fig. 6. Outline drawing of the profile of one of the craters of the Sikhote-Alin meteorite shower (by E. L. Krinov and S. S. Fonton).

thrown into the air and are attracted by the Earth's gravity. However, when meteoritic bodies have a large original mass that runs into scores or hundreds of thousands of tons, the region of delay is beneath the surface of the Earth, and what is left of the meteoritic body then strikes the surface of the Earth with the remaining cosmic speed. At the moment of impact this speed may be sufficient to emit a considerable quantity of heat energy and transform part of the meteoritic matter into heated compressed gas. As a result, at the point of impact, explosion of the meteorite and ground takes place.

Stanyukovich and Fedynsky (1947) and Stanyukovich (1950) established that when the speed of a meteorite falling on the surface of the Earth does not exceed 100 m per sec, an ordinary hole or pit is formed at the point of impact in soft ground, and the dimensions of the hole are comparable with the dimensions of the meteorite. However, when a meteorite falls at this speed on hard stony ground, both the meteorite itself and the ground break. When a meteorite strikes soft ground at an impact speed from 100 m per sec to 500 m per sec, it also breaks up. The meteorite fragments and the ground fly in all directions, resulting in a crater whose size exceeds that of the meteorite: the greater the impact speed, the larger the crater. When the speed is over 500 m per sec the size of the crater increases as the impact speed increases, but the mechanism of crater formation does not change qualitatively. However, when the impact speed exceeds 3 or 4 km per sec the picture changes sharply: a powerful blast spreads outward from the point of impact (as the center of explosion) and destroys the meteorite as well as the surrounding adjacent ground. At this speed a solid body acquires the properties of highly compressed gas, as the force of molecular cohesion is relatively small compared with the energy of the

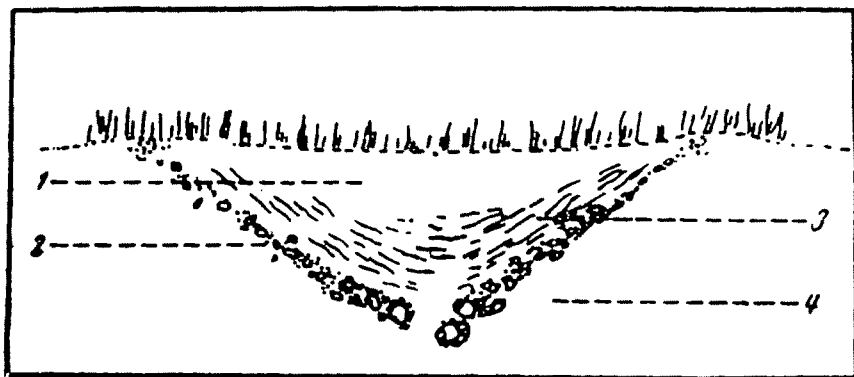


Fig. 7. Outline drawing of the profile of the Brenham meteorite crater (according to H. H. Nininger).

blast wave. The great quantity of the compressed gas immediately strives to expand leading to the explosion of the meteorite and the formation of a meteorite crater.

When the speed of the impact equals approximately 5 km per sec, the action of the entire destructive mass of the meteorite and the ground in the zone of the explosion amounts to the action of an equivalent mass of explosive material. But as the impact speed exceeds 60 km per sec, the explosive action of the meteorite mass and the adjacent ground will be 1000 times greater than the action of explosive material of the same mass. Thus, when large meteorites fall, craters of the two main types are formed: impact craters due to the mechanical destruction of the ground caused by the fall of large meteorites, and explosive craters due to the fall of giant meteorites. A characteristic feature of the impact craters is the great number of meteorite fragments they contain. Meteoritic fragments, original rock, and soft ground line the inside slopes of the craters. Moreover, the largest impact craters do not exceed several dozen meters in size, whereas it is doubtful whether the smallest explosion craters are less than a hundred meters in diameter.

The craters formed by the largest individual samples of the Sikhote-Alin meteorite shower (Krinov, 1956a, 1956b, 1959) are classical examples of impact craters. In the dispersion ellipse of this shower, 122 craters were found (not counting the small holes), of which 17 are from 10 to 26.5 m in diameter. A study of these craters showed that not a single one showed traces of explo-

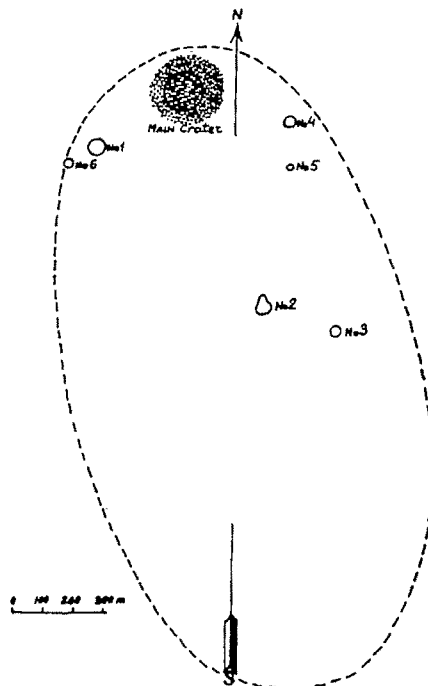


Fig. 8. Diagram of location of Kaali meteorite craters.

sion, such, for example, as elevated layers of original rock around the crater rim, fused individual fragments, and burnt pieces of rock. On the contrary, the rims of the craters were formed of the filling matter, such as broken rock and soft ground. On the inside slopes of all these craters, layers of meteorite fragments were discovered mixed with broken rock and soft ground (fig. 6). In addition, particles of meteoritic dust were discovered by magnet among the matter filling the crater. Thus, the morphological properties of the largest craters of the Sikhote-Alin meteorite shower are similar to the morphological properties of the small craters of the Kaalijarv group.

The Brenham (Haviland) meteorite crater in Kansas is probably an impact formation also (fig. 7). It is about 17 m in diameter but before excavation it was a depression that was hardly noticeable. When H. H. Nininger excavated the crater to a depth of 2 m, he discovered countless fragments of this remarkable stony-iron meteorite (pallasite) that changed over to an iron meteorite (octahedrite). The fragments were covered with earth, abundantly permeated with rust. The largest fragment weighed 39 kg; most of the fragments, however, had already been completely transformed into rust (Nininger and Figgins, 1933).

At present there are about a dozen craters throughout the world that have been reliably identified as meteorite craters. In almost every case there are groups of craters that include one or two craters which are larger than the rest. The groups of craters indicate that large and sometimes giant meteoritic bodies break up in the atmosphere and meteorite showers occur. At the same time, the presence of the craters of larger size in each group shows that they are explosion craters while the others in the group are impact craters.

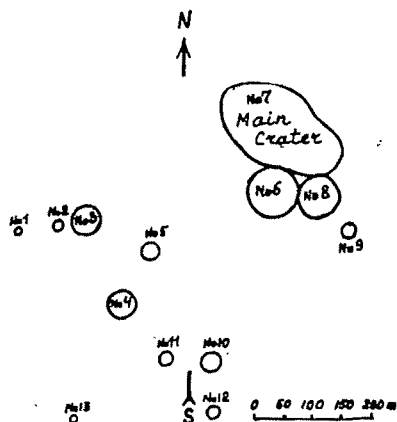


Fig. 9. Diagram of location of Henbury meteorite craters.

A map of the location of the Kaalijarv meteorite craters is shown in figure 8. The main crater is in the north-northwest section of the area while all the small craters are to the south-southeast of it. The relative locations of the craters prompts the conclusion that the meteoritic body moved from south-southeast to north-northwest. Under atmospheric pressure, it broke up into

parts. One of the fragments was so large that it reached the Earth's surface with the remaining cosmic speed. Hence, when it struck the ground there was an explosion and the meteorite crater was formed. That the main crater is of the explosion type is indicated by the layers of elevated dolomite that spread radially from the center and the presence of pieces of burnt dolomite. All the other fragments of the meteoritic body probably had a relatively small mass and therefore lost their cosmic speed at some altitude above the Earth's surface. They then fell according to the Earth's gravity, forming impact craters where they struck the ground. This explains the great difference between the size of the main crater and all the other craters. However, the difference in the sizes of the various small craters is relatively small, substantiating the conclusion that all the small craters (Nos. 1 to 6) of the Kaalijarv group are impact craters.

There is complete similarity between the regularity in distribution of the Kaalijarv craters, which clearly defines the dispersion of the separate meteorite masses and the isolation of the explosion craters, and the group of 13 Henbury craters in Australia, discovered in 1931 (Spencer, 1933). The main crater in the latter group, 220 and 110 m in diameter (there are probably two main closely connected explosion craters), is situated in the northeast section of the area and all the others, which are considerably smaller, are to the southwest of the main crater (fig. 9). Consequently, we may conclude that the meteoritic body in this case moved from southwest to northeast.

During the meteorite shower at Kaalijarv, besides crushing the layers of dolomite and forming craters, the smaller meteorites themselves split up into a multitude of fragments and meteoritic dust that have been preserved to this day in the matter filling the crater. It may be supposed that farther to the south-southeast still smaller samples fell, forming craters of correspondingly smaller size (fig. 8). Perhaps, on careful study of the locality, traces of such craters in the form of slight depressions may still be discovered. Lastly, further to the south-southeast, small individual samples weighing from a few grams or less to hundreds of kilograms must have fallen. The larger samples possibly lie preserved in the ground. It may therefore be assumed that on careful study of the locality with instruments such as mine-detectors they may still be found.

In conclusion it should be emphasized that the Kaalijarv meteorite craters are of outstanding scientific significance. A careful and thorough study of these formations will undoubtedly yield important data on the circumstances of the fall of giant meteorites and the nature and magnitude of the accompanying explosion phenomena. A study of the locality to the south-southeast of the craters with the help of the proper instruments may lead to the discovery of meteorite masses.

The craters of the Kaalijarv, the Tunguska fall and the Sikhote-Alin iron meteorite shower are the three outstanding phenomena in meteoritics within the territory of the Soviet Union.

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AN EARLY CRETACEOUS (HAUTERIVIAN) ANGIOSPERM FRUIT FROM CALIFORNIA

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ABSTRACT. A well-preserved fruit that may represent an extinct angiosperm of the family Icacinaceae, or a precursor of the family, has been found in the Ono formation of northern California associated with marine invertebrates of Hauterivian age. This section has earlier yielded a small transported flora consisting of an angiosperm of doubtful affinity, together with typically Neocomian conifers, ferns, and cycadophytes that appear to have characterized the vegetation of the adjacent shore area.

INTRODUCTION

Only a few older Cretaceous (Neocomian) sections have provided us with the remains of flowering plants. Most of those from California, Virginia, and Portugal are leaf impressions that can not be assigned with certainty to living taxa. Chiefly for this reason, some investigators have thought that they may not even be valid records of ancient angiosperms. Thus it is highly significant that a well-preserved angiosperm fruit was found recently in the Ono formation, northern California, in a section that has previously yielded an angiosperm leaf impression of doubtful affinity associated with a typically Early Cretaceous flora (Fontaine, *in* Ward, 1905). By a curious coincidence, a similar find of a slightly older (Valanginian) fruit was reported at approximately the same time from Vaulcluse, southern France (Chandler, 1958). It is to be hoped that these discoveries of angiosperm fruits will stimulate the search for additional material in Lower Cretaceous and even older rocks. Finds of this sort may be expected to increase now that geologists are directing more detailed attention to the finer structures of ancient sediments.

Interpretation and identification of an isolated specimen of the sort recorded here presents a number of difficulties. Most important is the fact that no (or very few) comparable living angiosperms can be expected in rocks of this age. Even in the latest Cretaceous and earliest Tertiary (Danian-Ypresian), many of the genera based on fruits and seeds are extinct, though most of them can be related to living families. Further, only a few fruits are as yet known from strata of Cretaceous age and most of them do not assist in evaluating the affinities of the present material. Yet special mention must be made in this connection of a species of *Phytocrene* from the Upper Cretaceous Raritan formation of New York (Scott and Barghoorn, 1957), and of *Paleophytocrene* from the Eocene London Clay (Reid and Chandler, 1933) and from the Eocene Clarno of Oregon (Scott, 1954), for they aid in some measure in evaluating the present fossil. Finally, the preservation of the unique specimen described here leaves some room for doubt as to certain of its structures, and the transparent plastic in which it had to be embedded for sectioning causes reflections that make it difficult to assess some of the finest details.

It is a pleasure to record here our indebtedness to Drs. Michael A. Murphy and Peter Rhodda who turned over the fossil to us for study. Owing

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to their detailed geologic studies in the Ono region, the fossil fruit has a well-defined stratigraphic position.

GEOLOGIC OCCURRENCE

The thick section of fossiliferous Lower Cretaceous rocks exposed in the Ono region 20 miles southwest of Redding, California is the type area for the stratal unit previously termed the Horsetown group or formation and recently redefined as the Horsetown stage (Murphy, 1956). The lower part of the section is represented by the Rector formation, which ranges from 20 to 400 feet in thickness. This sandstone and conglomerate unit is markedly transgressive on the igneous and metamorphic rocks of the bordering Klamath Mountains at the west. The Ono formation, which has yielded the fossil fruit, conformably overlies the Rector. It is approximately 4200 feet thick and is composed chiefly of mudstone and nodular limestone, interrupted by two coarse clastic tongues of graywacke and conglomerate. The section is exposed as a gently southeast-dipping homocline which is complicated by many small, and a few large faults.

The fossil fruit was recovered from a limestone nodule in calcareous grit associated with mudstones in the lower part of the Ono formation, about 500 feet below the base of the Roaring River conglomerate tongue. The locality is $3\frac{1}{2}$ miles southwest of Ono, near the head of a small branch of Roaring River. The exact site is 1500 feet N 65° W of the southeast corner of sec. 17, T. 30 N., R. 7 W., Ono quadrangle, U. S. Geol. Survey, 1952 ed. The locality is in the *Neocraspedites aguila* zone, the lowest biostratigraphic unit of the Horsetown stage (Murphy, 1956). Other diagnostic fossils of this zone include *Potamides diadema* Gabb and *Plicatula variata* Gabb. Among their usual associates are *Nucula gabbi* Stanton, *Turbo festivus* Anderson, and *Tessarolax bicarinata* (Gabb). Fragmentary plant remains are common in these strata. Plants previously reported from this section have been referred to the following genera (Fontaine, in Ward, 1905): *Cladophlebis*, *Ctenopteris*, *Sagenopteris*, *Dioonites*, *Ctenophyllum*, *Cephalotaxopsis*, *Sphenolepidium*, and *Acaciaephyllum*.

TAXONOMIC DESCRIPTION

? FAMILY *Icacinaceae*

Genus *Onoana* nov.

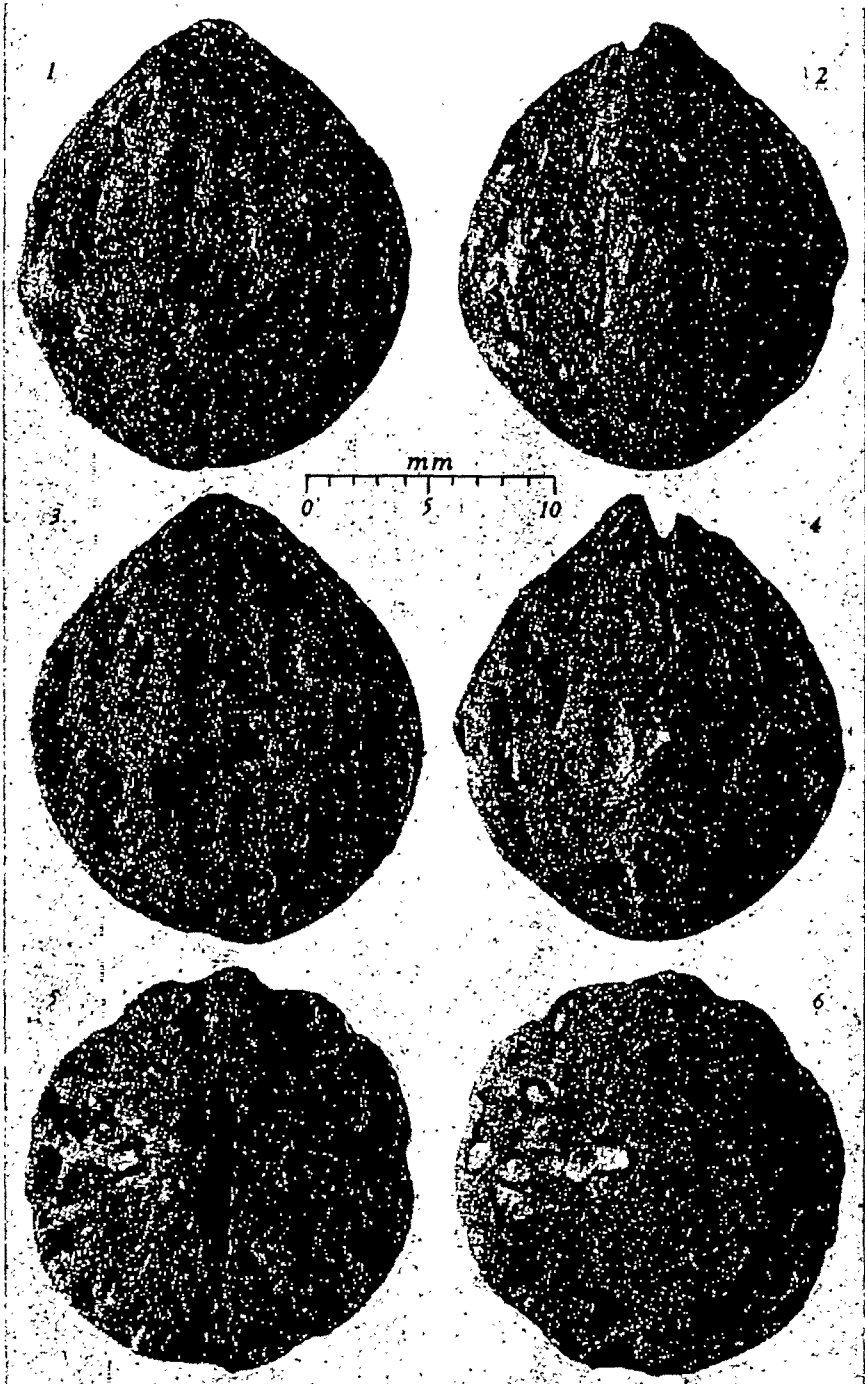
Onoana californica n. sp.

(Pl. 1, figs. 1-6; pl. 2, figs. 1-2)

Diagnosis.—Endocarp apparently obovoid, with a median longitudinal fissure at the narrow end giving an obscure bisymmetry. Endocarp 20 mm long, with a transverse diameter of 15 mm. Wall thick, having numerous deep, large pits with closed inner ends which do not form protuberances on the locule surface, those near the proximal end traversing the wall obliquely, those at the distal end perpendicular to the surface of the endocarp. Solitary locule.

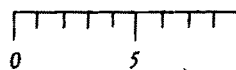
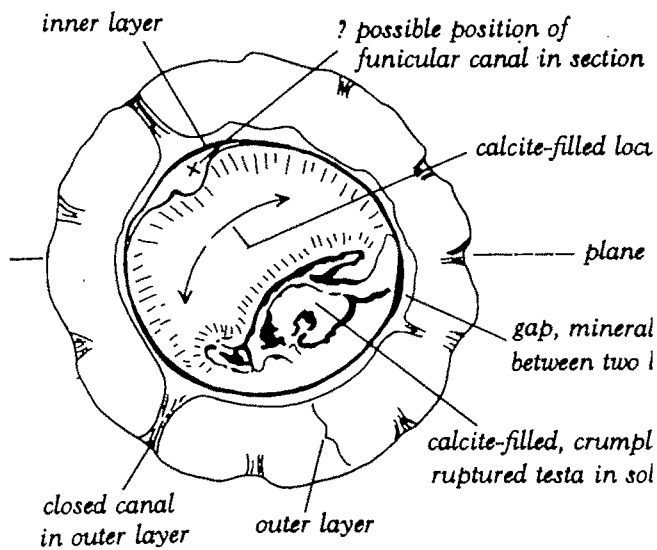
Description.—Endocarp woody, thick walled, with a finely fibrous surface on which the fibers are chiefly aligned longitudinally. Pointed-obovoid, with a slight bisymmetry at the pointed, proximal (?) end owing to a median longi-

PLATE 1



External views of *Onoana californica* Chandler and Axelrod.

PLATE 2

Transverse section of *Onoana californica* Chandler and Ax

tudinal fissure (pl. 1, figs. 2, 4, 5). The fissure extends for one-third of the length of the endocarp on one side (pl. 1, fig. 4), and for a shorter distance on the other (pl. 1, fig. 2).

The whole surface shows deep, coarse, irregularly scattered pits particularly well exposed owing to abrasion of the surface. That abrasion has occurred is indicated by the finely frayed margin of the endocarp when seen in section under the microscope. In surface view the pits are circular to linear in outline (pl. 1, figs. 1-6), and the majority are elliptical. Most of the circular pits are at the presumed distal end and the linear pits at the proximal end. This variation of form suggests that if they are due to hair bases, as in *Stizocarya* from the London Clay (Reid and Chandler, 1933), those nearest the proximal end traversed the wall obliquely, whereas those at the distal end pierced it in a perpendicular direction in such a manner that all hairs were directed upwards. A slight apparent variation in the distribution of the pits may be original but may also be due to varying degrees of abrasion on different sides of the specimen. It is possible, but cannot be ascertained beyond doubt, that there may have been a small round depression at the distal (?) end of the endocarp; if so, abrasion caused it to merge with adjacent pits.

The surface pits are clearly visible in the transverse section of the endocarp, which passes through the deepest part of several, and shows that they extend to the limit of an outer thick layer of the endocarp wall but never penetrate to a thin inner layer. Where the section has cut near to the edge of a pit, it passes for only a short distance into the outer layer (pl. 2, figs. 1-2), the depth varying with the position of the section in the pit.

The transverse section of the endocarp has been cut at the middle. It shows a compact outer layer about 3 mm thick, which appears to be formed of parenchyma with radially aligned cells at least towards the exterior, giving the finely frayed edge mentioned above. A thin inner part is composed of transversely aligned cells. It has become separated from the outer 3 mm and forms a thin compact inner layer surrounding the locule. Separation of the two layers may be due to natural maceration and is emphasized by mineralization of the gap now seen between them. The surface of separation is slightly uneven; in one place, at least, the two layers are connected.

The fruit appears to show one locule enclosing a contracted and crumpled seed to one side of it, the space left by the shrinkage of the seed being filled with white calcite. Only remnants of the testa are preserved and are represented by disrupted fragments in which no cells can be distinguished. There may be evidence of a funicular-canal on the opposite side of the locule to the seed, but this is very doubtful as it is seen only in transverse section and may merely represent a bulge in the loosened locule lining.

It was necessary to consider whether two locules were present, one without a seed (filled with white calcite), the other less developed, with a shrunken seed, and broken remains of a thin septum between the two locules. This view was discarded because the presumed septum is so thin and it also bears no relationship to the plane of symmetry. It is therefore regarded as part of the testa of the collapsed seed.

All hard woody endocarps are provided with some means by which the germinating embryo can emerge. There seems little doubt that in *Onoana* germination was by partial separation of two valves along the proximal fissure leaving a gap for the radicle.

Affinity.—In the case of an endocarp of such antiquity as the present one, the question naturally arises as to whether it shows relationships to the woody ranalian alliance. There appear to be no grounds for regarding the fossil as ranalian but rather as representing a plant that had evolved well beyond that level.

The presumed unilocular endocarp with wall partially pierced by canals recalls the section Phytocreneae of the family Icacinaceae. In some species of *Phytocrene* itself, and in the extinct genus *Stizocarya*, the canals do not penetrate the inner part of the wall, whereas in *Phytocrene* they may be distributed irregularly. In both these genera, and in *Paleophytocrene* (Reid and Chandler, 1933), they traverse the wall in a perpendicular direction. By contrast, in the Ono fossil some of the canals, and especially those at the proximal end of the endocarp, appear to traverse it obliquely as described above. Thus it seems necessary to establish a new genus, for which the describer (Chandler) proposes the name *Onoana*. The points above indicated as doubtful make it advisable to refer this genus only provisionally to the Icacinaceae, though bearing in mind that it may represent a precursor of the family.

It is greatly to be hoped that the discovery of additional material in the Ono section may afford more definite evidence of the morphology of this unique fruit, especially as regards the course of the funicle which in the Icacinaceae lies in the plane of splitting, and also of the position of the placenta, and the character of the seed.

Collection. British Museum (Nat. History) No. V. 42334. Since the largest fossil seed collections are in the British Museum, the California specimen has been added to them so that as new finds are made this and other ancient angiosperm fruits can more readily be studied.

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HOW OLD ARE THE ANGIOSPERMS?

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ABSTRACT. Available evidence has earlier led to the inference that ancient angiosperms originated in moist tropical upland regions during Permo-Triassic time.

Recent arguments, which purport to show that there was a much briefer interval between the time of origin and appearance of angiosperms in the record, and that they evolved in lowland areas, are not consistent with evidence from morphology, evolution, paleoecology, or paleoclimate.

INTRODUCTION

The preceding paper (Chandler and Axelrod, 1960), which describes one of the oldest undoubted angiosperm fruits on record, adds a little more evidence to the few facts now available which can be used to assess the antiquity of flowering plants. At present there are two opposing views concerning the probable age of the alliance. One group has felt that data favor the inference that primitive flowering plants, representing taxa that are extinct but which gave rise to alliances (families, orders) ancestral to modern ones during the Jurassic and Early Cretaceous, probably were in existence by Permo-Triassic time (Axelrod, 1952, 1960; Camp, 1947; Eames, 1960; Němejc, 1956, Melville, 1960). More recently, Scott, Barghoorn, and Leopold (1960) documented a case for an origin during the Middle Mesozoic. The arguments which they have marshalled for such a recent history for flowering plants are in no wise decisive. The inadequacies of the major criticisms that they have leveled at inferences that favor the occurrence of ancient flowering plants in moist tropical upland regions during the Permo-Triassic are sketched here in the same order that they attacked the original theory (Axelrod, 1952). In addition, the principal weaknesses of a theory that visualizes only a brief unrecorded lowland history for the phylum are also noted.

PRE-CRETACEOUS ANGIOSPERMS

Axelrod (1952) reviewed most of the records of Jurassic and Triassic angiosperms reported up to that time and concluded that some of them probably were correctly assigned to the phylum (also see Thomas, 1936). This was considered to indicate that the alliance was already in existence during the later Triassic, some 40 million years prior to the first Cretaceous records. Hence the origin of the group was believed to have occurred somewhat earlier, probably during the Permo-Triassic transition. This conclusion that the alliance probably has considerable antiquity was not new but had been suggested earlier by Thomas (1936) on the basis of presumed rates of evolution in the group, and by Camp (1947) from morphological evidence of known Cretaceous angiosperms. More recently, Němejc (1956), Eames (1960), and Melville (1960) have summarized additional morphological data which suggest that the phylum is an ancient one and that it probably was in existence by the close of the Paleozoic.

On the other hand, Scott, Barghoorn, and Leopold (1960) take the extreme position that Krausel (1956) has already enunciated: Because all

records of pre-Cretaceous angiosperms are suspect, they do not provide a means for evaluating the antiquity of the group. Their reanalysis of some of the previously reported pre-Cretaceous "angiosperms" is most welcome and deserves careful study by anyone who is sufficiently bold to describe another pre-Cretaceous flowering plant. They conclude (p. 285) that "... there has not yet been described a pre-Cretaceous plant whose angiospermous affinities are unequivocal". Like Krausel, they reach this decision because nearly all of the morphological features which characterize angiosperms are also represented in other alliances. Vessel-less wood indistinguishable from that attributed to primitive living angiosperms occurs in the extinct cycadeoids; vessels characterize most angiosperm woods and have also developed in six other phyla of vascular plants; leaves with reticulate venation occur not only in angiosperms but also in the Gnetales, ferns, and seed ferns; stomata of angiosperms may resemble those of cycadophytes; even the flower is difficult to define in such a way that it excludes the inflorescences of cycadophytes; and angiospermy was essentially attained by the Caytoniales and some early Mesozoic seed ferns. Thus they properly point out that until angiosperm ancestors are identified there is uncertainty as to the extent of the morphological gap between flowering plants and their predecessors. "Only double fertilization and endosperm development seem to be unique angiospermous achievements" (p. 296).

(1) They are no doubt correct when they assert that "there has not yet been described a pre-Cretaceous plant whose angiospermous affinities are unequivocal" (p. 285). However, their criticisms of all pre-Cretaceous angiosperm records are nullified because they have not demonstrated that these plants are nonangiospermous: they first have to show (somehow) that the previously reported pre-Cretaceous angiosperms did not have double fertilization and endosperm before they can be rejected as valid angiosperm records. Obviously, all presently known pre-Cretaceous "angiosperms" will always comprise unequivocal records. In fact, until we are fortunate enough to find seeds which were mineralized under extremely exceptional conditions we never will have an undoubted pre-Cretaceous angiosperm. We realize that the pre-Cretaceous fossils now in hand are not decisive as evidence for angiosperms, yet Scott, Barghoorn, and Leopold have given us no real reason to doubt that at least some of them are ancient angiosperm taxa (families, orders, possibly classes) that have been long extinct, and that they actually do provide us with evidence of the plexus from which the alliance diverged.

Their argument clearly lacks conviction because all of the angiosperm characters (apart from endosperm development and double fertilization), which they reject as evidence for recognizing the existence of previously reported flowering plants (p. 285-287), they also believe were present in early angiosperm evolution.

(2) Scott, Barghoorn, and Leopold believe that angiosperms diverged from an ancestral alliance during the Middle Mesozoic. This is difficult to understand because they present no evidence which might lead to the assumption that flowering plants were even in existence at this time. On the contrary, they emphatically conclude that all previously reported records of pre-Cretaceous angiosperms are suspect or at least unequivocal. They particularly emphasize

that during the past decade intensive palynological studies have failed to turn up any authentic angiospermous pollen in pre-Cretaceous rocks which . . . "makes it quite unlikely that angiosperms could have persisted in upland regions from the Paleozoic to the Cretaceous without having contributed microfossils to sedimentary basins (p. 297)." Using their own argument, we may appropriately note that, if it is "quite unlikely" that angiosperms were in the uplands prior to the Cretaceous, then it is practically certain that they were not in the lowlands: otherwise we should have Jurassic pollen. Nowhere do Scott, Barghoorn, and Leopold attempt to explain why we have no records of these plants which they maintain were evolving in the Middle Mesozoic.

UPLAND ORIGIN FOR ANGIOSPERMS

To account for the paucity of angiosperms in the pre-Cretaceous lowland record several investigators have suggested that they probably evolved in upland regions.¹ As reasons supporting such a view had not been presented, Axelrod (1952) developed three arguments favoring the inference, all of which have been rejected by Scott, Barghoorn, and Leopold (1960).

Upland Record Not Preserved

Practically all of the known pre-Cretaceous plant record was accumulated at or close to sites of deposition in lowland basins, notably in lakes, swamps, floodplains, and deltaic to nearshore marine areas. Because any pre-Cretaceous sediments which were deposited in upland basins could not have persisted for any long period of time owing to erosion, the probability of finding ancient angiosperms which may have been preserved there is very low.

To this suggestion, Scott, Barghoorn, and Leopold bring the argument that, if early angiosperms were in the uplands for an interval lasting from the Permo-Triassic to the Early Cretaceous, we should at least expect to find some evidence of pollen grains preserved in lowland record. They point out that, as water is an effective medium of transport from highland to lowland areas, pollen grains—owing to their small dimensions (silt size) and high resistance to chemical and microbiological attack—should be in the lowland record if they had existed in the uplands at this early date. A number of examples of long-distance transport are cited to support the argument. They note (p. 290) that during the past decade the emphasis on palynology "has resulted in the examination of thousands of samples of sediments of Mesozoic age from the major geographic regions of the earth including many from the tropics; but authentic pre-Cretaceous pollen has not yet been reported." They conclude (p. 297) that . . . "the common intermingling in sediments of pollen derived from plants growing in diverse habitats, including uplands, makes it quite unlikely that angiosperms could have persisted in upland regions from the Paleozoic to the Cretaceous without having contributed microfossils to sedimentary basins."

¹ Since the word "upland" is not precise it may have led Scott, Barghoorn, and Leopold (1960) and others as well to misunderstand the concept. It is to be emphasized that the term was never intended to connote high montane summits or the upper zones of mountains. On the contrary, the writer has visualized rolling hilly tracts and the lower to middle slopes of mountainous terrain in the ancient tropics as an upland environment. We grant that the word lacks precision, yet in the present case it has much in its favor because we can speak about ancient angiosperm evolution only in general and vague terms.

(1) First, it is appropriate to note again that although Scott, Barghoorn, and Leopold doubt that angiosperms could have existed in the uplands for the 60-million-year period from the Permo-Triassic to the Early Cretaceous without having contributed to the pollen record, they nonetheless postulate that angiosperms were evolving in the Middle Mesozoic, which is only 30 million years later. Curiously, they provide no explanation for the absence of pollen records during the 40-million-year period of evolution which they believe occurred prior to the Early Cretaceous. Obviously, if the pollen argument has validity, and they believe it does, then it must mean either (a) that the whole phylum is of post-Jurassic age, or (b) that the absence of pollen from the record is not a crucial argument for rejecting an hypothesis that visualizes the emergence of the phylum in Permo-Triassic rather than in Middle Mesozoic time.

(2) The absence of undoubted pollen grains (though some have been reported) in the record from the Late Paleozoic to the Early Cretaceous may be owing to any one or all of the following four factors:

(A) Most pre-Cretaceous angiosperms may have produced pollen that was not yet wholly distinctive of the alliance. In all phyla of vascular plants different parts of the plant body show evolution toward increased complexity, as illustrated by the evolution of woody tissues, stems, sporangia and spores, fronds, leaves, flowers, etc. In some taxa, however, primitive structures may persist for long intervals of time. Thus certain primitive living angiosperms still have open carpels (*Degneria*), vessel-less wood (*Trochodendron*), and foliar stamens (*Himantandra*).

Angiosperm pollen grains show morphological evolution into more complex forms, and the more primitive living alliances have also preserved ancient pollen morphology. For instance, some ranalian taxa still produce pollen that is generally regarded as primitive. Those with 1-sulcoidate apertures (*Austrobaileyaceae*, *Cannellaceae*, *Degneriaceae*, *Himantandraceae*, *Myristicaceae*) and those that are nonaperistate (*Lauraceae*) are in this category. The fact that nonaperistate grains, which are represented in the ranalian alliance as well as in other groups (*Cannaceae*, *Juncaceae*, *Marantaceae*, *Musaceae*, *Zingiberaceae*), could be mistaken for nonsaccate grains of conifers, and that those with 1-sulcoidate apertures could be taken for certain pteridophytes or gymnosperms, is a significant point. If pre-Cretaceous angiosperms were largely producing "gymnospermous" pollen we might well regard them as coniferous. In fact, it is to be noted that although some investigators have described pre-Cretaceous pollen (see records discussed by Scott, Barghoorn, and Leopold, 1960, p. 285-287), they believe that several of them represent gymnosperms. The belief that pollen grains underwent considerable morphological evolution during pre-Cretaceous time seems a reasonable assumption, although Scott and co-authors appear to favor the view that angiosperm pollen scarcely evolved at all during the pre-Cretaceous history of the phylum. In view of the nature of the evolution of other plant structures this would be a most remarkable phenomenon if it could be proven.

(B) The pollen of pre-Cretaceous angiosperms may not yet have evolved an exine sufficiently resistant to permit easy preservation. For example, genera

of such families of the woody ranalian plexus as Lactoridaceae, Lauraceae, and Himantandraceae have a very thin exine and hence are generally not preserved even in the Tertiary record. A number of others have grains that are not resistant to chemical (acid) or microbiological attack, for instance, Cannaceae, Juancaceae, Marantaceae, Zingiberaceae, and Thurniaceae, and they also are but rarely preserved. Thus it seems more reasonable to infer that many pre-Cretaceous angiosperms also produced pollen that had not yet developed an exine sufficiently strong to withstand either the rigors of long transport or later chemical and microbiological attack, rather than to suppose that most of them had pollen grains as resistant as those which lived much later in the history of the alliance.

(C) Every higher (and lower) category comes into existence in some local area. During its early evolution, which may involve some tens of millions of years, populations are comparatively small, and the alliance maintains a generally restricted occurrence. In view of the inferred small size of early angiosperm populations and their spotwise distribution (Axelrod, 1952, 1960), the possibility of contributing pollen to the sedimentary record was greatly reduced in pre-Cretaceous as compared with Middle Cretaceous and later times when angiosperms were nearly everywhere dominant. Clearly, local distribution and small numbers would tend to limit their entry into the pre-Cretaceous lowland record, whether in the Permo-Triassic or the Middle Mesozoic transition.

(D) Early angiosperm evolution may have occurred in moist tropical regions, which no longer exist as land areas, and hence all records of their early history may be lost forever. The evidence that links the origin of the alliance to tropical rather than to temperate regions has been discussed elsewhere (Bews, 1927; Axelrod, 1952, 1959, 1960). In brief, the phylum is basically adapted to moist tropical forests today; the derived alliances commonly comprise the more specialized taxa of both tropical and extratropical regions; modern distribution patterns show that three-fourths of all angiosperm families are primarily adapted to tropical regions; and the fossil record shows that they migrated from lower to higher latitudes as they initially invaded lowland areas during the Early Cretaceous.

A considerable body of evidence indicates that during the pre-Cretaceous, and into the Late Cretaceous and Early Tertiary as well, angiosperms migrated extensively over land areas which have since subsided (Axelrod, 1960). The evidence supporting this view lies in the present and past distributional relations of angiosperm families and genera that are confined chiefly to the moist tropics of America, Africa, and Australasia. Today there are 54 pantropic families common to these regions, and they comprise the larger and more characteristic alliances of the tropics. These intertropical ties are strengthened when we note that an additional 125 families, although represented in the temperate and drier regions by derivative taxa, attain optimum diversity and development in the moist tropics and are chiefly of pantropic occurrence. Further, a number of tropical families have discontinuous occurrences: 12 of them link the American and African regions, 8 the tropics of America and Australasia, and 16 are common to the tropics of Africa and Australasia. Significantly,

there is good fossil evidence to show that an even larger number of families and genera were common to these tropical regions in the past and that the discontinuous and endemic occurrences of the present day are more recent (Axelrod, 1960, p. 247-249).

These relations can not be explained by postulating migration around the higher latitudes during the Cretaceous and Early Tertiary: those areas were occupied by temperate climates during this long interval, and in pre-Cretaceous time as well. Trans-tropic migration is therefore required in order to account for both the present and past distribution of tropical taxa. Migration appears to have been across land areas that occupied the West Indian Ocean, the mid-Atlantic, and greater Melanesia. The geological evidence which indicates that these are continental—not oceanic—regions has been summarized in some detail elsewhere (Axelrod, 1960). Clearly, if early angiosperms evolved in some ancient tropical land area which has subsequently foundered, we could not expect to recover any records of them.

(3) The authors point out that "the occurrence, due to parallel development, of many of the advanced features of angiosperms in (other) taxa raises the possibility that, whatever the relationships of these elusive ancestors, they had already evolved in their structural organization features now characteristic of the angiosperms (p. 296)". This is a reasonable suggestion, yet it raises a problem relating to the site of early evolution that Scott and others (1960) have not considered: if forerunners of the alliance that had already evolved typical angiospermous features were living in the lowlands during the Middle Mesozoic, as they believe, then we might reasonably suppose that the record would already have provided evidence of the gradual emergence of the phylum from this proangiosperm plexus. However, Scott and others not only carefully note that all previously reported pre-Cretaceous "angiosperms" may well belong to other phyla but nowhere do they report any Middle Mesozoic ancestral plants that "had already evolved in their structural organization features now characteristic of the angiosperms". The fact that angiosperm ancestors have not yet been recovered from the abundant lowland record seems best explicable by the inference that they probably were living in the distant uplands, in areas too remote for preservation in the lowland record. If they were living in the lowlands, as Scott and others (1960) believe, then why is it that we still have no records of these ancestral plants which in most ways were already angiospermous?

Cliseral Relations

A second argument supporting the idea that early angiosperms may have existed in upland regions during pre-Cretaceous time comes from the cliseral relations of sequences of fossil floras (Axelrod, 1952, 1960). They show that often the more specialized and advanced taxa, as well as younger floras, were present in the uplands of a region long before they entered the lowlands to replace the older flora.

Scott and others concede that the record provides agreements with the general thesis as well as some exceptions; I disagree with some of their supposed exceptions, but this is no place to argue details. They then state that if angiosperms had been in the uplands from the Permian to the Cretaceous a

widespread major climatic deterioration presumably would have been required to initiate their invasion of the tropical lowlands to displace the older Gymnophyte Paleoflora (1960, p. 291-292). As they point out, paleoclimatic consideration of plants as well as other groups of organisms indicate that conditions remained generally equable over most of the world during the Early Cretaceous.

(1) These criticisms are based on a misinterpretation of the significance of the basic idea, which they concede is largely true: the record does support the inference that higher categories, such as flowering plants, often have evolved in upland areas. Nowhere in the original theory (Axelrod, 1952), or in an extension of it (Axelrod, 1960), has a worldwide climatic change been called upon to account for their entry into the lowland record.

(2) Present evidence suggests that it took flowering plants all of Early Cretaceous time to assume dominance over the lowlands throughout the world (Axelrod, 1959). They are encountered first in the lowland record at lower-middle latitudes in the Neocomian, they reached generally middle to high-middle latitudes in the Aptian, they appeared at high latitudes in small numbers only in the Albian, and did not dominate there until Early Cenomanian time. The gradual poleward migration of angiosperms during this 35-million-years interval may reflect gradual climatic change. If Early Cretaceous climate was slightly cooler than that of the Jurassic—and some evidence suggests that it was—angiosperms may well have responded by migrating into the lowlands. However, replacement of the Gymnophyte Paleoflora may be owing to other factors as well, biologic, ecologic, etc. The argument which Scott and others (1960) present obviously does not discount the likelihood that they may have evolved in the uplands long before they entered the lowland record.

Diversity of Upland Environment Promotes Rapid Evolution

Evolutionary theory (Simpson, 1953; Stebbins, 1950) indicates that diversity of environment in the uplands would tend to favor the rapid evolution of early angiosperms. This environment would not only include a diversity of physical conditions owing to varying slope and climatic relations but the accompanying biotic diversity in these areas would also help promote the rapid evolution of the group during its early history. Scott, Barghoorn, and Leopold attempt to discount the idea of an upland origin for angiosperms in several ways.

(1) As noted earlier, their argument with respect to the absence of pollen of pre-Cretaceous angiosperms that may have been living in the distant uplands is irrelevant. If they were not in the uplands, they certainly were not in the lowlands either: from their interpretation of the evidence we may just as well conclude that the entire history of the phylum is post-Jurassic. As we have seen, at least four factors probably contribute to the absence of recognizable pollen grains in the pre-Cretaceous record.

(2) They state that "flowering plants have . . . found the tropical lowlands favorable for diversification; floras of the tropical rain forest are probably the richest plant assemblages known. . . ." (p. 292).

The argument that angiosperms have diversified in the tropical lowlands is true, but only in part. The bulk of the flora that now comprises the moist

lowland tropical rain forest is relict. The areas occupied by the rain forests of America, Africa, and Indomalaya comprise refugia for numerous ancient taxa that were gradually confined to these areas during the middle and later Tertiary as climates became cooler and drier over regions of their former occurrence. The present luxuriant rain forests are analogous to the temperate mixed hardwood forests of northeastern Asia and North America that are surviving relicts of the Arcto-Tertiary Geoflora.

Scott, Barghoorn, and Leopold (1960) present no evidence to indicate flowering plants initially evolved in the lowlands. On the contrary, some data clearly lead to the inference that they did not. In the first place, it is necessary to note that, owing to the nature of later Cenozoic climatic change, the lowland tropical rain forest now lives in an environment that is hotter and wetter than it has ever been. It is the forests on the bordering slopes (uplands) that appear to survive under a climate more like that of Eocene and earlier (pre-Cretaceous) times. Thus it becomes understandable that many of the more primitive living angiosperms persist in upland areas. This applies to the rare woody ranalian relicts in New Caledonia-Fiji and to a host of woody ranalian plants that live in the mountains of southeastern Asia, centering in the subtropical valleys of Yunnan and upper Burma (see Takhtajan, 1957, for examples). Since they are ancient bradytelic taxa, they probably have persisted under generally similar conditions for long periods of time. Thus the upland tropical to subtropical environments in which they occur may well resemble, at least in a general way, those under which angiosperms originated. This suggestion is consistent with taxonomic studies (Camp, 1947, 1952, 1956), which indicate that of the genera that have a fairly wide altitudinal range in the tropics, the more primitive living species usually occupy the mountain slopes, not the hot humid lowlands. It would thus appear that there has been considerable evolutionary deployment into the hot and humid tropical lowlands, not early evolution there.

(3) Scott and others (1960) note that Richards (1957, p. 346), in his fine discussion of modern tropical forests, shows that the tall, luxuriant tropical rain forest of the lowlands is replaced by other communities in the uplands that are also evergreen, but lower in stature, simpler in structure, and floristically poorer. The purely tropical flora is left behind and gives way to a montane flora in which many of the genera, or even the species are temperate. Five major zones of vegetation, often sharply delimited, can be distinguished in the tropics, and the general features of their altitudinal zonation appear similar in both the New and Old Worlds. From these valid observations of modern tropical forests, Scott and others then conclude that this five-zoned altitudinal distribution . . . "must have existed in the past. The existence of this zonation suggests that, had the early angiosperms been restricted from the Permian to the Cretaceous to upland habitats of sufficient altitude to furnish environmental diversity of effective contrast to that of the tropical lowlands, the resultant flora would have developed a more temperate aspect rather than the lowland character to which the available evidence points (p. 293)".

1(A) These assertions with respect to the existence of several vertical zones of tropical forests in the past are at variance with paleoclimatic evidence. Dur-

ing the time under consideration, the Earth had no regional polar, tundra, taiga, desert, or mediterranean climates. The margins of the moist tropics lay near Lat 45° N and S during the interval when flowering plants are supposed to have been evolving, whether from the Middle Mesozoic (Scott and others) or the Permo-Triassic (Axelrod). At these times the tropical and temperate zones were much broader than they are today. As latitudes now supporting tundra, polar and taiga climates were temperate, the tropical zone must have been somewhat cooler (though still tropical) than it now is in order to maintain the normal heat budget of the earth. Obviously, under such conditions vertical zonation in the tropics would have been much less than it is today, even if extreme topography like that of the present existed, and there is ample evidence to show that it did not.

(B) Their assertions with respect to the altitudinal zonation of tropical forests in the past are also at variance with paleobotanical evidence. There is no basis for projecting the existence of the present five zones of tropical forests into the pre-Cretaceous. No doubt there were zones wherever there was sufficient altitude, but studies of the evolution of Tertiary Geofloras into modern communities clearly demonstrate that altitudinal zonation of communities developed as new subclimates appeared owing to intense orogeny at the close of the Tertiary. Generalized plant communities were then segregated climatically into more specialized associations adapted to new subclimatic zones (for example, see Braun, 1935; Axelrod, 1950, 1957). To suppose that the present altitudinal zonation in the tropics "must have existed in the past" is obviously erroneous. The present is not always the key to the past. Communities and climates have evolved in time, and modern forest zones do not give us a clue to those of the ancient past.

(C) As for the temperate aspect which they think that upland angiosperms would have developed during the pre-Cretaceous, this idea has already been discussed (Axelrod, 1952, 1960). Plants in the high uplands (i.e. highlands) and also those toward middle latitudes near the margins of the ancient tropics certainly were evolving under the influence of more temperate conditions: it was here that the remote, pre-Cretaceous ancestors of taxa that ultimately gave rise to the Arcto-Tertiary and Antarcto-Tertiary Geofloras evolved. In other words, some of these pre-Cretaceous upland angiosperm populations were adapted to both tropical and warm temperate climates, and from them evolved alliances adapted to more temperate areas. Analogous relations exist at present in the upper montane rain forest in the tropics, where typically temperate and tropical taxa still live in proximity.

RATE OF EARLY EVOLUTION

Having noted that all records of previously reported angiosperms are unequivocal and asserted that the absence of angiosperm pollen from pre-Cretaceous rocks makes it unlikely that the phylum could have been evolving at a time as remote as the Permo-Triassic, Scott, Barghoorn, and Leopold (1960) then conclude that angiosperms were evolving rapidly just prior to their appearance in the record, apparently in the Middle Mesozoic. "If several of these (angiosperm characters), e.g. vessels, reticular leaf venation, [etc.], had al-

ready evolved in precursors, the evolutionary steps that differentiated flowering plants may not have been very great, and the geologic time required for their diversification not extreme (p. 296)." They allude to great diversification and wide distribution attained by herbaceous dicotyledons during Miocene and later time as an example of rapid evolution to support the idea that angiosperms may have had only a brief pre-Cretaceous history.

(1) From an evolutionary standpoint there is no doubt that several angiospermous features were already evolving in precursors of flowering plants, or that the evolutionary steps which finally differentiated true flowering plants probably were not very great. In this connection, an excellent paper by Mayr (1960) deals with the origin of higher categories, much of which seems applicable to the problem in hand.

But the example which Scott, Barghoorn, and Leopold present for asserting that the emergence of full-fledged angiosperms did not take much time has no bearing on the problem of rate during their early evolution. They intimate that rates of evolution in herbs which were evolving 100 million years *after* the first well-documented angiosperms appeared may represent the rate when the phylum was initially differentiating. Earliest angiosperm evolution involved the emergence of a wholly new way of life, the most successful ever achieved by land plants. Initially, it adapted the alliance to living more successfully in the moist tropics, a zone that unquestionably has been the most stable and persistent of all terrestrial environments. By contrast, the herbaceous dicotyledonous evolution to which Scott, Barghoorn, and Leopold refer only represented adaptive radiation into the more rigorous environments that developed during the middle and later Cenozoic over areas of the former occurrence of more widely distributed mesophytic ancestral herbs of closely similar character. In this connection we may also recall that herbs have an annual life cycle as compared with the earliest primitive angiosperm trees (or shrubs), which certainly required a much longer time to mature: woody ranalian taxa not only grow very slowly as compared with most other woody angiosperms, they also require a longer time for flowering and fruiting. Scott, Barghoorn, and Leopold give us no reason to believe that the rate of diversification of herbs from mesophytic ancestors, which involved only minor change on an already well-established pattern, provides us an index to the rate of diversification of early flowering plants at a time when major categories (orders, classes, etc.) were being blocked out.

There is no basis for supposing that the rate of herbaceous dicotyledonous evolution since the Oligocene indicates the time required for the emergence of full-fledged angiosperms. Measuring downward from the basal Cretaceous, the 30 million years involved would place their origin in the Late Triassic. If it took twice as long, as seems more probable, then angiosperms would have been in existence in the Permian. Evidence has already been assembled (Simpson, 1953; Axelrod, 1952) which suggests that the emergence of a category of the sort that we are considering here requires fully 50-60 million years. Scott, Barghoorn, and Leopold have not demonstrated that angiosperms emerged from their ancestral alliance any more rapidly.

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OXIDATION IN HIGH TEMPERATURE PETROGENESIS

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ABSTRACT. A study has been made of a variety of metamorphic and magmatic rocks to determine how oxidative processes are reflected in their mineral assemblages. In this study particular attention is paid to solid solutions.

Field and experimental evidence agree with theory as to the responses of ferromagnesian solid solutions to compositional changes of the coupled gas phase. Typical of these responses are the increases shown by the ratios $\text{Fe}_2\text{O}_3/\text{FeO}$ and $\text{MgO}/(\text{MgO} + \text{FeO})$ with increasing P_{O_2} .

Attention is also directed to the consequences of the normally low values of $\text{P}_{\text{O}_2}/\text{P}_{\text{H}_2\text{O}}$ to gaseous transport by bodily flow and diffusion in regional metamorphism.

Examples of oxidative and related processes are drawn from regionally metamorphosed iron formations of Quebec and the Lake Superior region, from numerous contact metamorphic deposits, from the extrusives of the San Juan region of Colorado, and from other magmatic provinces. A thermodynamic unity of response to oxidative processes is shown by these different rock types.

INTRODUCTION

Viewed in its broadest sense the process of oxidation¹ is the fundamental reaction of petrogenesis. Ironically in the case of the highly oxidized crust of the Earth, consisting largely of oxygen and metallic ions of fixed valence state, this is apt to be forgotten. In the science of metallurgy and in the study of metallic ore deposits the effects of oxidative processes are often obvious because of the conspicuous interactions of oxide and metallic phases. However, in "ordinary" rocks as well, oxidative reactions manifest themselves in subtle and often intriguing ways. This is especially true of rocks which contain phases, such as the ferromagnesian silicates, which show extensive solid solubility of the ferrous iron and magnesian components.

The effects of oxidation may be expected to assume importance in any environment that contains substantial amounts of elements with variable valence states. Rocks falling into this category are very abundant and include representatives from nearly every petrogenic environment. Of peculiar interest in this respect are the meteorites and other extraterrestrial bodies now increasingly under investigation. Evidence of reactions between the condensed phases of these bodies and various gases may be of great significance in the study of their gravitational and temperature history. Equally interesting are the terrestrial iron-rich representatives of regionally and contact-metamorphosed rocks and the magma series and their consolidated equivalents.

This paper will be confined to the study of terrestrial metamorphic and magmatic rocks. The object here is to define more precisely the role in petrogenesis of high temperature oxidative reactions connecting gases and phases showing solid solubility, but some consideration will also be given to magmatic differentiation. Although the simultaneous consideration of such broad categories as metamorphic and magmatic rocks may seem overambitious, it is hoped that such a treatment will reveal the underlying thermodynamic unity of oxidative processes in those widely varying rock types.

¹ Here the term oxidation is used in a sense which includes reduction as well.

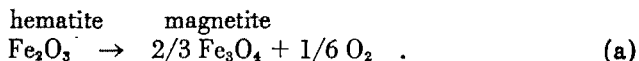
OXIDATION IN REGIONAL METAMORPHISM

Environmental conditions.—In order to understand the effects of oxidation in regional metamorphism it is necessary to consider the conditions which particularly characterize this environment. Geologic evidence leads to the conclusion that, in contrast with contact metamorphism, relatively uniform conditions of pressure and temperature over wide regions and isolation from the atmosphere are characteristic.

One of the most interesting questions with respect to this environment concerns the role of an oxygen-containing gaseous phase. Evidence that such a phase must arise frequently during the course of development of most dynamothermally metamorphosed rocks is the presence of healed and partially healed fractures of every age. These as well as intergranular imperfections seem to assure the presence of at least some gas at every stage. It would seem that only the presence of a liquid phase under high pressure could prevent the appearance of a gas. However, even under these conditions oxygen would exert its influence through the medium of the liquid solution.

Mineral indicators of P_{O_2} .—In the gaseous phase oxygen exerts a partial pressure along with such gases as H_2O , CO_2 , H_2 , and CO . The relations between these gases and the coexisting solid phases are of great consequence to the ultimate mineralogy. Among the most significant mineral assemblages are those containing magnetite and hematite. The significance of these oxides lies in their wide occurrence and that they may, when associated, define P_{O_2} as a univariant function of the temperature. Under these circumstances the system is said to be buffered with respect to oxygen. Over the greatest part of the temperature range of regional metamorphism the actual value of P_{O_2} for the system hematite-magnetite is vanishingly small, of the order of 10^{-40} to 10^{-10} atmospheres. An important consequence of these low pressures is that only small quantities of oxides need react to bring about relatively great changes in P_{O_2} . The practical aspects of such systems are attested by the fact that they have been used (Eugster, 1957) to control P_{O_2} in experimental work.

The pertinent reaction for the hematite-magnetite association is the following:



The equilibrium curve for this reaction is shown in figure 1.² This curve puts limits on the partial pressure of oxygen in rocks which contain one or more of these oxides in equilibrium with the gas. Thus, if we know that a magnetite-bearing rock crystallized in the neighborhood of 500°C, we see from figure 1 that P_{O_2} was probably less than 10^{-18} atmospheres. Conversely if the same rock contained hematite, we should suspect that P_{O_2} was greater than 10^{-10} atmospheres. Of course these conclusions require that the magnetite and hematite concerned be pure compounds as written in reaction (a). This requirement is more apt to be met in hematite than in magnetite, as the latter may under certain conditions dissolve considerable amounts of MgO or other oxides depending on their concentration in the system and the temperature.

² This curve is calculated from the equation $\log P_{O_2} = \frac{-119240 + 67.62T}{2.303 RT}$ (see Kubaschewski and Evans, 1958).

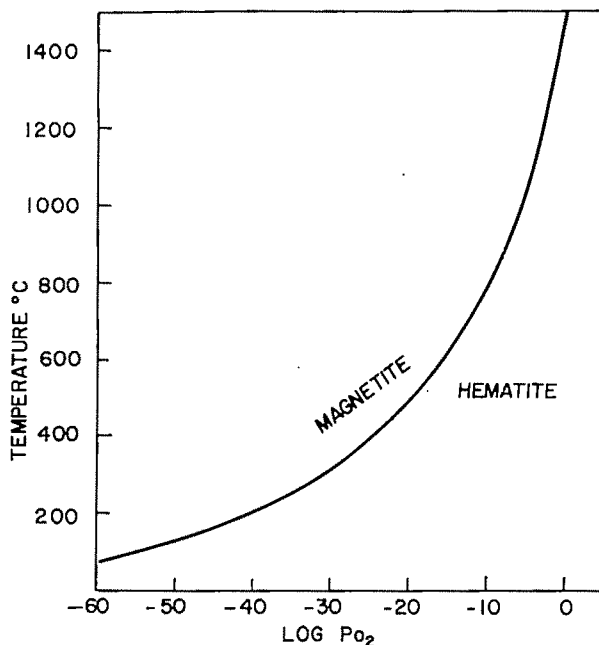
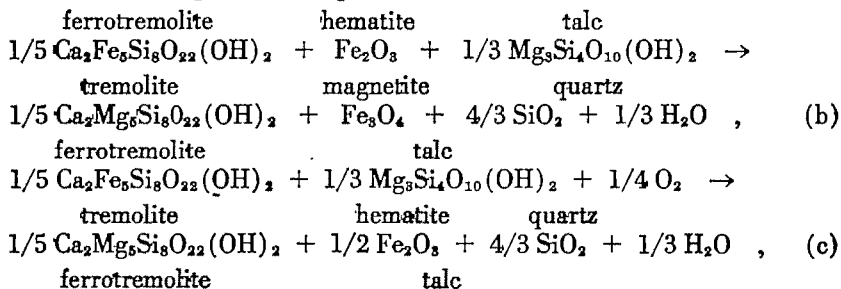


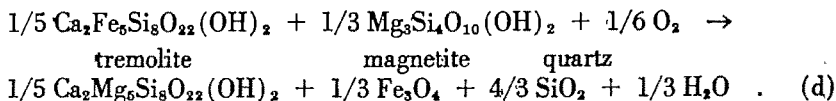
Fig. 1. Stability fields of magnetite and hematite.

Correlation of P_{O_2} with crystalline phases may also be extended to the silicates which form solid solutions. Consider the following mineral assemblages which occur in the Quebec iron formation (Mueller, 1960):

1	2	3
actinolite	actinolite	actinolite
talc	talc	talc
magnetite	hematite	magnetite
hematite	dolomite	quartz
calcite		
dolomite		
quartz		

We wish to compare these three assemblages to see how the atomic ratio $MgO/(MgO + FeO)$ of actinolite is related to the different values of P_{O_2} implied by the different oxides present. The pertinent reactions are as follows:





It should be noted that the end members of the solid solution series actinolite as well as talc, quartz, and water enter into all three reactions with the same stoichiometric coefficients, and that in fact the three reactions differ only by multiples of reaction (a). All of the mineral components which enter into the three reactions occur in assemblage 1, and from this consideration it is apparent that in a thermodynamic sense all three reactions take place in this assemblage without the appearance of additional phases. However only reaction (c) may occur in assemblage 2 and only (d) in 3.

According to thermodynamics these reactions have corresponding equations involving the law of mass action. Since, however, tremolite and ferro-tremolite as such do not occur in these rocks, but rather as mutually dissolved components of actinolite, their concentrations in this solid solution play an important role in the equations of equilibrium. This concentration may be expressed as $\text{MgO}/(\text{MgO} + \text{FeO}) = X_{\text{act}}$. Because the actinolite solid solution is probably approximately ideal, it may be shown (Mueller, 1960) that the two following equations provide a comparison of oxidizing conditions in assemblages 2 and 3 with those in the complete assemblage 1:

$$\frac{P_{\text{O}_2}^{1/4}}{(P'_{\text{O}_2})^{1/4}} = \frac{X_{\text{act}} (1 - X'_{\text{act}})}{X'_{\text{act}} (1 - X_{\text{act}})} \quad (1)$$

and

$$\frac{P_{\text{O}_2}^{1/6}}{(P''_{\text{O}_2})^{1/6}} = \frac{X_{\text{act}} (1 - X''_{\text{act}})}{X'_{\text{act}} (1 - X_{\text{act}})} \quad (2)$$

Here the single-primed symbols refer to assemblage 2, the double-primed ones to 3, and the unprimed to 1. It may be seen that these equations compare the composition of actinolite in the three assemblages in terms of P_{O_2} . In deriving these equations it was assumed (on the basis of other evidence) that $P_{\text{H}_2\text{O}}$ and P_{CO_2} as well as the temperature were essentially the same where the three assemblages were formed, and that the environment differed only with respect to P_{O_2} .

Equations (1) and (2) refer a system in one oxidation state (assemblage 2 or 3) to a thermodynamically more restricted system in another oxidation state (assemblage 1). In terms of oxidation the reference system here is actually that involved in reaction (a) which is a subsystem to assemblage 1. That is, assemblages 2 and 3 fall in the stability fields of hematite and magnetite respectively, and the composition of actinolite varies accordingly.

The mineral assemblages 1, 2, and 3 illustrate the response of silicates containing ferrous iron and magnesium to different oxidizing conditions, the effect being an increase of the equilibrium concentration of magnesium with increasing oxygen pressure. How this is reflected in other assemblages of the Quebec iron formation is shown in figure 2.

Normally, however, another process plays a part in the response of iron-bearing silicates to varying P_{O_2} . This is the increase in the ratio $\text{Fe}_2\text{O}_3/\text{FeO}$ with increasing P_{O_2} . Since, however, P_{O_2} is related to P_{H_2} by the reaction H_2O

Here again there has been little or no change in the degree of oxidation, and apparently P_{O_2} was kept high enough throughout metamorphism to prevent the formation of ferrous silicates. It is interesting in this connection that the occurrence of contemporaneously crystallized cummingtonite and hematite is very rare both in the Lake Superior region and in Quebec. Where this association does occur in the Quebec iron formation, the cummingtonite is found to be Mg-rich in accord with the principle already illustrated for actinolite. This feature is also shown by figure 2.

The relative stabilities of hematite and magnetite in regional metamorphism is sometimes a subject of speculation. It is obvious that this problem can be meaningful only in relation to figure 1, although in regional metamorphism the high pressures acting on the solid phases will alter this picture somewhat. It is also clear that in many cases the solubility of such oxides as MgO in magnetite may have to be considered. However, hematite is known to persist, and, as indicated above, iron formations seldom show any obvious reduction during progressive metamorphism, whereas great losses of H_2O and CO_2 often characterize these rocks under the same conditions. This differential degassing has a ready explanation if the equilibrium concentrations of the gases are taken into account. Bowen (1940) and Weeks (1956) have discussed a variety of univariant metamorphic reactions involving CO_2 . From these reactions it may be seen that the equilibrium pressures of CO_2 in the carbonate-silicate reactions are usually of the order of 1 to 10^3 atmospheres at ordinary metamorphic temperatures. Similarly P_{H_2O} seems to be of the same general magnitude for many metamorphic dehydration reactions (Fyfe, Turner, and Verhoogen, 1958). These partial pressures are enormous when compared with the equilibrium values of P_{O_2} for reaction (a) as shown by figure 1. An important consequence of this is the following: If the equilibrium P_{H_2O} is only one atmosphere (a conservative value) over the hydrous silicates of a given rock, the ratio $P_{H_2O}/P_{O_2} \approx 10^{20}$, if magnetite and hematite are also present and acting as buffers. If magnetite alone is present this ratio may be even greater. Thus if the gases escape by mass movements along openings such as fractures, they will be lost in the ratio of their concentration or P_{H_2O}/P_{O_2} . Thus dehydration will greatly dominate reduction. The same argument also applies to P_{H_2}/P_{H_2O} , which will also generally be low as demanded by the equilibrium constant for the decomposition of water.

If on the other hand gases are lost by diffusion along intergranular boundaries, the relative rates of diffusion of the different species will play a part. If dm/dT is the material transferred across a unit area perpendicular to X per unit time,

$$\frac{dm}{dT} = -D \frac{dc}{dx} \quad (3)$$

is an expression for gaseous diffusion. Here D is the coefficient of self-diffusion, and dc/dx is the concentration gradient. The following relation also holds:

$$D = 1/3(\bar{v}\lambda) ,$$

where $\bar{v}$ is the mean molecular speed, and λ is the mean free path. Now since

$\bar{v}$ is a function only of the temperature and λ depends on the total molecular concentration, D is practically independent of the concentration for a gas with a low partial pressure. However, dc/dx is a function of c . Consequently dm/dT of gases such as O_2 and H_2 might be expected to be very small in regions buffered by such systems as magnetite-hematite, although it would be somewhat higher for hydrogen than for oxygen. As a result of these relations it may be concluded that oxide systems, once established in a particular part of a rock, are resistant to change by oxidation unless exposed to such over-riding effects as contact with the atmosphere or large volumes of highly oxidizing fluids. This, then, appears to be a logical explanation for the persistence in metamorphic rocks of distinct layers of minerals of various oxidation states.

Also it seems possible that conditions might sometimes arise under deep-seated metamorphism, such as might be encountered in the granulite facies, when P_{O_2} might be very low, perhaps corresponding almost to the stability field of metallic iron. Under these conditions P_{H_2} will be substantial, and consequently the differential loss of hydrogen by minerals might be an important factor.

Thus it seems that certain elements such as oxygen may be transported in significant quantities only if they are combined with another element to form a compound of high equilibrium partial pressure, for example, water. This aspect of diffusion has been discussed by Ramberg (1952).

OXIDATION IN CONTACT METAMORPHISM

General features.—Physico-chemical conditions in the vicinity of igneous intrusive bodies are likely to be characterized by a greater irregularity than those of regional metamorphism. Near the contact steep gradients in temperature, stress, and fluid pressures may be expected. Temperatures near these molten bodies of rock will be higher than any except those encountered under the highest grade of regional metamorphism. Pressure, on the other hand, may be considerably lower, as the majority of recognized contact phenomena probably occurred under relatively shallow conditions. This is especially true for the extensive group of contact rocks of the western United States discussed in this paper. Many of these rocks are regarded on the basis of geologic evidence to have formed at less than a mile below the surface (Lindgren, 1928).

One of the most characteristic features of contact deposits is the widespread associated metasomatism which sediments near the contact have undergone. Heavy metals, silica, alumina, and sulfur have been introduced in great quantities at the expense of original sedimentary constituents such as CO_2 . It should not be assumed, however, that metasomatism is any more prevalent in contact metamorphism than in regional metamorphism; it is simply true that the original unaltered sediments are more easily recognized for comparison in the case of contact metamorphism.

Contact metamorphic phenomena undoubtedly accompany every type of intrusion ranging from plutonic to shallow depths. It therefore might be expected that a sequence of contact phenomena that is the result of varying degrees of influence by the atmosphere should be realized. Increasing evidence of oxidation accompanied by loss of CO_2 should therefore characterize this se-

quence in general. The possible change of mineralogic assemblages and the change of composition of individual mineral species as reflections of these varying physico-chemical conditions in the sequence of environments is our concern here.

Characteristics of contact metamorphic mineral assemblages.—The contact metamorphic rocks which have received the greatest amount of attention are those associated with economic mineral deposits, especially in the western United States. The type of intrusion associated with these contacts is typically a small stock or a dike of Tertiary age. The intruded sediments were usually relatively unmetamorphosed before the intrusion.

Some of the most spectacular contact effects are achieved in carbonate-rich sediments. The chemical system involved in such contacts is usually dominated by the following components: CaO , MgO , FeO , Fe_2O_3 , SiO_2 , H_2O , and CO_2 . It is seen that this system is identical to that of the carbonate iron formation discussed in the previous section on regional metamorphism. It will therefore be instructive to compare the two types of rocks. An additional important component, which often occurs in contact rocks, is Al_2O_3 . This component appears to be essential in the formation of epidote, a common contact mineral. Other components such as S, Cu, etc., account for economic minerals, but these will not be considered here since they enter into the silicates in only small amounts.

One of the most common types of contact metamorphic assemblages in the western United States is that depicted in figure 3. The components of this figure are the same as for figure 2 except that Al_2O_3 is considered together

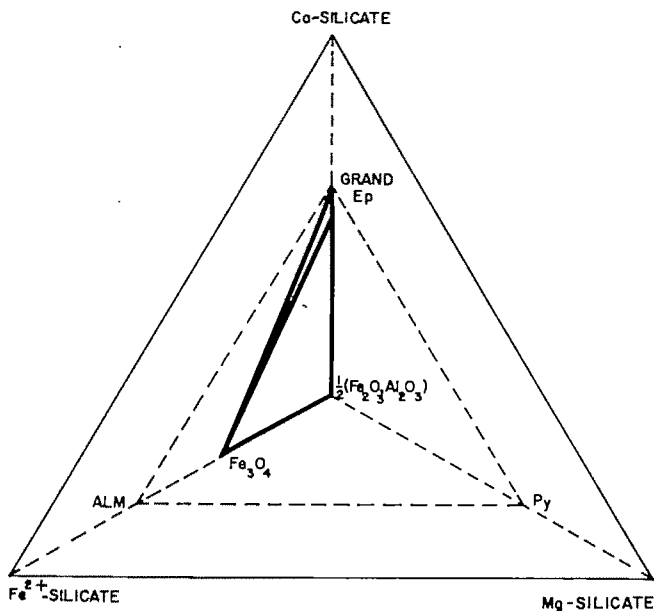
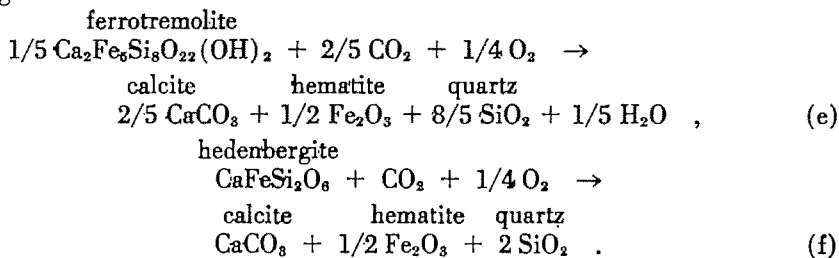


Fig. 3. Tetrahedron showing typical magnesium-poor contact metamorphic mineral assemblages. Mineral symbols are as follows: alm = almandine, py = pyrope, grand = grandite (andradite-grossularite), and ep = epidote.

with Fe_2O_3 . The plane Alm-Py-Grand represents the garnets with the respective end members almandine, pyrope, and grandite (andradite-grossularite) as corners. Typical representatives of the assemblage epidote-grandite-magnetite are widespread in the Giffton-Morenci district of Arizona (Lindgren, 1905). The assemblage as shown in figure 3 is magnesium-poor. The exclusion of the possibility of the association grandite-epidote-hematite in figure 3 is only apparent because this figure does not differentiate between Fe_2O_3 and Al_2O_3 and does not show the component H_2O . The latter assemblage is, in fact, common and illustrates the fact that diagrams such as figure 3 should be regarded only as aids to presentation. Few if any conclusions regarding equilibrium mineral association may be drawn from them. Figure 3 does, however, illustrate the highly oxidized nature of this assemblage. Analyses of garnets from these assemblages show them to be nearly pure andradite (Lindgren, 1905). The widespread occurrence of these assemblages in the western United States is in harmony with the shallow nature of the contact phenomena.

If Mg is an important component, additional assemblages similar to those of figure 4 will result. Figure 4 is based on the same components as figure 3 but shows in addition the solid solutions actinolite and Ca-pyroxene. The small distorted tetrahedron of figure 4 shows the assemblage garnet-Ca-pyroxene-actinolite-hematite. Such minerals as quartz and calcite, although not shown in figures 3 and 4, are possible additional phases. The actual position of the tie line connecting Ca-pyroxene and actinolite in figure 4 is taken from a representative occurrence of this assemblage at Iron Mountain, Missouri (Allen and Fahey, 1952, 1956). The atomic ratio $\text{MgO}/(\text{MgO} + \text{FeO})$ is essentially the same in both minerals and is equal in this case to approximately 0.72. The relation $(\text{MgO}/(\text{MgO} + \text{FeO})) \text{ Ca-pyroxene} = (\text{MgO}/(\text{MgO} + \text{FeO})) \text{ actinolite}$ was also found for these coexisting species in the Quebec iron formation (fig. 2). This seems to imply either that the two occurrences were formed near the same temperature or that the distribution of Mg and Fe^{2+} is not very sensitive to temperature.

One of the most interesting things about figure 4 is the actual magnitude of $\text{MgO}/(\text{MgO} + \text{FeO})$. To see what is involved here we consider the following reactions:



Since ferrotremolite and hedenbergite are components of actinolite and Ca-pyroxene respectively, it is obvious that the composition of the latter minerals may be expected to be complex functions of the temperature and the partial pressures of H_2O , CO_2 , and O_2 . Thus the actual positions and slopes of the tie lines of figure 4 also depend on these variables. Reactions (e) and (f) indicate

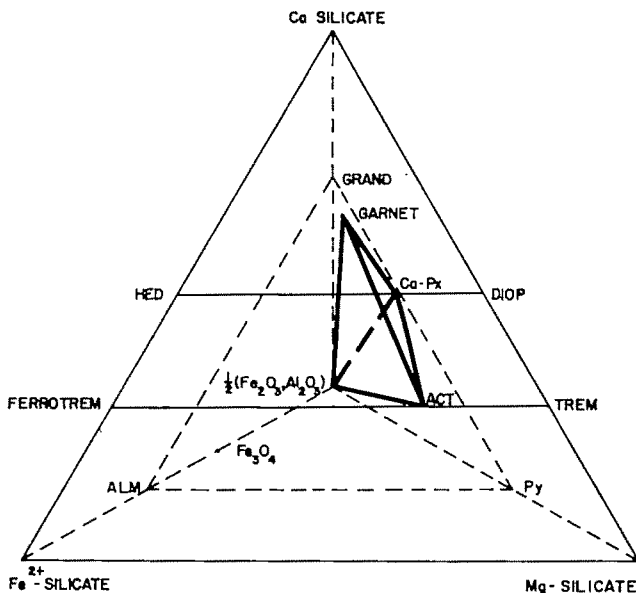


Fig. 4. Tetrahedron showing typical magnesium-rich contact metamorphic mineral assemblage. Mineral symbols are as follows: alm = almandine, py = pyrope, grand = grandite (andradite-grossularite), hed = hedenbergite, diop = diopside, ferrotrem = ferrotremolite, trem = tremolite, Ca-px = Ca-pyroxene, and act = actinolite. Compositions of the coexisting minerals are taken from Allen and Fahey (1952, 1956).

that, if the temperature and P_{H_2O} and P_{CO_2} are held constant, increasing P_{O_2} leads to a decrease of the equilibrium concentration of Fe^{2+} in actinolite and Ca-pyroxene. However, if P_{H_2O} , P_{CO_2} and T are allowed to vary, their individual or combined effects may cancel out the effect of P_{O_2} . Thus each mineral assemblage must be studied in terms of the total environment. However it is still possible and even probable that in a large number of occurrences of a given assemblage there will be a statistical correlation between $MgO/(MgO + FeO)$ and P_{O_2} . The statistical nature of such a correlation would not be due to any caprice on the part of nature but would rather conform to definite and expectable variations in the other variables.

An examination of the literature of contact metamorphism seems to indicate that such a correlation does exist. Unfortunately, adequate descriptions of coexisting minerals and the compositions of those minerals are rare in the literature. However, existing information all points to a relation similar to that shown by the Quebec iron formation. In the assemblages such as those of figure 4, which contain hematite and ferromagnesian silicates, the latter tend to be magnesium-rich. The assemblage of Iron Mountain, Missouri has already been referred to. Also in many of the ore deposits of New Mexico (Lindgren, Graton, and Gordon, 1910), where specular hematite is very widespread, the Ca-pyroxene and actinolite associated with specularite are usually described as "diopside" and "tremolite" or as being virtually colorless (and thus implying low iron). Table 1 shows the occurrence of contact metamorphic minerals in New Mexico by districts, as presented by Lindgren, Graton, and Gordon. The

TABLE 1
Minerals of contact-metamorphic deposits of New Mexico by district (after Lindgren, Graton, and Gordon (1910))

	calcite	quartz	garnet	epidote	wollastonite	diopside	tremolite	specularite	magnetite	pyrite	chalcopyrite	galena	zincblende	molybdenite	Remarks
Elizabethtown	+		+	+		+	+	+	+	+	+				scapolite and pyrrhotite present
Cimarroncito	+		+	+				+	+	+	+				gold present
Ortiz			+							+	+				biotite present, vesuvianite reported
San Pedro	+		+			+	+	+		+	+		+		
Magdalena	+	+				+	+	+	+	+	+	+			
Jones Camp									+						
Jarilla	+	+	+	+		+	+	+		+	+		+		
Organ	+	+	+	+		+		+	+	+	+		+		bismuth mineral present
Modoc	+			+								+	+		
Tres Hermanas	+	+	+			+						+	+		only oxidized zinc ores present
Hanover	+	+	+	+	+	+	+	+	+	+	+	+	+	+	hedenbergite, ilvaite present
San Simon	+	+	+	+	+	+				+	+				
Apache No. 2	+		+		+					+	+				scheelite present
Hachita (Copper Dick)	+		+			+				+	+				

table does not necessarily imply that the minerals coexist. The relatively highly oxidized character of these deposits is clearly indicated by the mineralogy that corresponds to figures 3 and 4. The writer knows of no instance in the literature where ferromagnesian minerals rich in ferrous iron are described as coexisting with hematite, although such associations have a theoretical possibility of occurrence by certain combinations of variables.

Although ferromagnesian minerals coexisting with hematite tend to be poor in ferrous iron, those coexisting with magnetite are frequently rich in this ion. As examples of the latter we have the magnetite-pargasite-hedenbergite-tactites described by Holser (1950) from the Phillipsburg region, Montana, and magnetite-hedenbergite-cumingtonite assemblages from New Mexico (Allen and Fahey, 1957).

It would seem from this cursory examination that the whole subject of the relationships of the silicates to the oxides, sulfides, and other ore minerals of contact metamorphic deposits needs re-examination in the light of modern theoretical and experimental methods.

OXIDATION IN MAGMATISM

Oxidation in differentiating and consolidating magmas as related to environmental complexities.—If an attempt is made to imagine the possible variations of physico-chemical environment in magmatism, it is apparent that a very great variety of such environments with respect to oxidation are possible. This will apply especially to magmas which consolidated eventually to hyalite or extrusive rocks. The partial pressure, or more properly, the activity of oxygen may be expected to play an important role in magmatic differentiation wherever iron is a major constituent; but even after consolidation of magmas, oxidative reactions between crystalline phases and gases, especially those derived from, or escaping to the atmosphere, may be expected to work significant modifications in the mineralogy.

In considering the influence of variables such as P_{O_2} on the history of magmas it is well to keep in mind the differences between the possible compositional variability of crystals and liquids. As may be seen by consideration of the many reactions between solids and between solids and gases in metamorphism, crystals have a somewhat restricted latitude of compositional range as compared with liquids. The variability in crystals tends to take the form of well-defined series of solid solutions. For example, Ca-pyroxene may often be considered as a simple solution of Mg and Fe^{2+} end members. Therefore the only possible response to oxidative processes of this mineral series is a change in the ratio $MgO/(MgO + FeO)$. Correspondingly large changes in the ratio Fe_2O_3/FeO may be brought about only by the simultaneous substitution of an ion such as Na^+ for Ca^{2+} . However, in a mineral such as hornblende, as we have seen, change of Fe_2O_3/FeO is also possible by a simultaneous change in the hydrogen content.

Because of their disordered state silicate melts are not thus restricted, and the mutual solubilities of almost all major rock-forming oxides extends over wide ranges of composition. Thus many paths of crystallization are possible along the liquidus during early stages of crystallization. As crystallization pro-

gresses, however, the available paths become more limited due to the simultaneous crystallization of a number of minerals and lead eventually to a small number of univariant paths on which the compositions of the liquid and the coexisting crystals are functions of such variables as T , P_{H_2O} , P_{CO_2} , and P_{O_2} . This is well illustrated in the experimental system $MgO-FeO-Fe_2O_3-SiO_2$ to be discussed later.

As mentioned above, after consolidation the magmatic rock is subject to continued alteration. This is especially true for siliceous extrusives such as rhyolite, which suffer extensive explosive disruption and fracturing. In these rocks residual fluids and atmospheric gases penetrate along every fracture, and a new mineralogy may develop as a consequence.

The mineralogy of the San Juan extrusives.—One of the most thoroughly studied magmatic provinces is that of the San Juan region of Colorado. Of special importance are the papers by Larsen and Cross (1956) and Larsen, Irving, Gonyer, and Larsen (1936, 1937), which contain a wealth of information on many aspects of magmatism, and especially such as involve the effects of oxidation and loss of volatiles on the mineralogy.

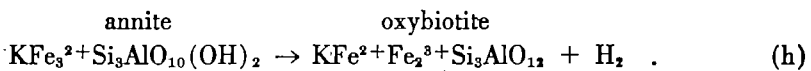
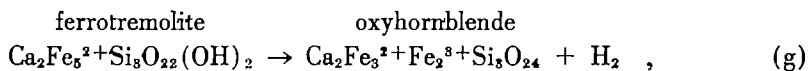
In the San Juan region extensive pyroclastics, flows, and shallow intrusives ranging from basalt to rhyolite developed during Tertiary time. These rocks present to the inquiring mineralogist an almost infinite variety of natural experiments in silicate chemistry. Single flows show evidence in the form of phenocrysts of magmatic differentiation at depth. These phenocrysts also bear witness to subsequent changes in the composition of dissolved volatiles during extrusion. The groundmass mineralogy reflects still later phenomena. Finally there is evidence of extensive reaction between late crystals of fractures and vesicles and gas phase.

One interesting observation made by Larsen, Irving, Gonyer, and Larsen (1936) is that the pyroxene phenocrysts of pyroxene andesites are higher in iron than those of quartz latites and rhyolites. This tendency is opposite to that noted by Larsen and Draisin (1948) in the plutonic rocks of the batholith of southern California and also to that noted by Chapman and Williams (1935) in the White Mountain magma series. Although Larsen considered this trend in the San Juan rocks to be at variance with experimental data of silicate systems, it is really not inconsistent with such data when proper account is taken of oxidation.

Most of the rocks of the San Juan volcanic series are conveniently classified as basalts, latites, quartz latites, and rhyolites, although most transitional varieties may be found. The most abundant minerals are olivine, clinopyroxene, approaching pigeonite, orthopyroxene, augite, several varieties of hornblende and biotite, plagioclase, sanadine, quartz, tridymite, cristobalite, and a variety of iron oxides. Olivine and pyroxene are naturally more abundant in basalts, but several varieties of pyroxene also occur in the rhyolites, and olivine is found as phenocrysts in rocks that contain quartz in the groundmass.

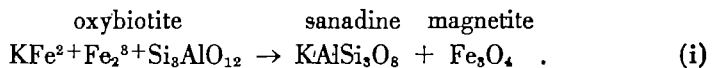
The ferromagnesian minerals that crystallized at depth, as represented by phenocrysts, are similar in properties to corresponding plutonic minerals. These unaltered minerals derived from greater depths are best seen in parts of

flow which have reacted least with the gases escaping from the magma or derived from the atmosphere. For example, hornblende in the black glass at the base of some flows is green, whereas the red porous vesicular parts of these flows have basaltic hornblende. A pair of such hornblendes from the Alboroto rhyolitic quartz latite were observed to be identical in composition except that the basaltic hornblende contained little water and its iron was largely ferric. As might be expected, the hydroxyl-bearing ferrous iron phenocrysts such as biotite and hornblende show the greatest evidence of reaction with the residual silicate melt and the escaping gases. As Larsen and others (1936) proved from the chemical analyses, these phenocrysts are oxidized to oxyhornblende and oxybiotite in the lava flows, and every gradation between unoxidized and completely oxidized phenocrysts exists. The following are possible reactions in the formation of oxyhornblende and oxybiotite:



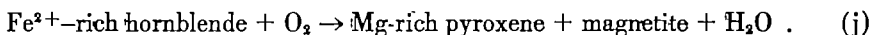
Oxidation by loss of hydrogen as shown is compatible with the chemical analyses which show a deficiency of water. However it is seen that loss of hydrogen alone results in the oxidation of only 2/5 of the ferrous iron in hornblende and 2/3 in biotite. Also it must be remembered that the ferrotremolite and annite components are usually mutually dissolved with other components such as tremolite and phlogopite.

From thermodynamic considerations it might be suspected that oxybiotite would be unstable relative to its reaction products as follows:



The common occurrence of magnetite with partially resorbed phenocrysts of oxybiotite seems to confirm that the right side of reaction (i) is usually favored. It seems probable that oxyhornblende also is unstable since like oxybiotite it usually shows strong resorption.

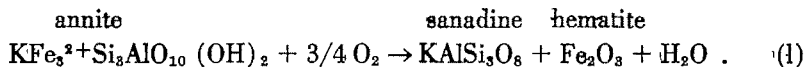
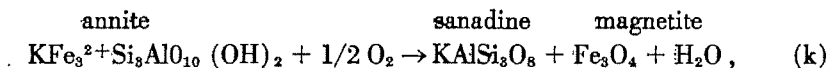
Larsen and others (1937) point out that the resorption of hornblende gives rise to a pyroxene much poorer in total iron than the hornblende from which it was derived. The sum of the oxidation reactions undergone by hornblende may be roughly represented as follows:



We see here again the same mechanism which was previously observed in the various metamorphic rocks. Similarly the same process may at times yield secondary hornblendes and biotites which by their paler color indicate a lower Fe-content than the original phenocryst minerals. In the flows of the Hinsdale formation, for example, Larsen and Cross (1956) describe a biotite of the gas cavities which is much lighter in color than that of the phenocrysts. Also hornblende of low iron content ($\alpha = 1.628$, $\gamma = 1.645$) is present in these cavities.

Other descriptions of late-crystallizing, pale-colored biotites are common in the paper by Larsen and Cross.

From these facts we may trace a complex and interesting series of events beginning with the crystallization of ferrous iron-rich phenocrysts at depth. On extrusion of the magma these phenocrysts are partially oxidized to oxybiotite and oxyhornblende by loss of H_2 to the atmosphere. Because of the inherent instability of these oxidized minerals, they are subsequently resorbed into the residual melt and reappear as oxides and Mg-rich pyroxenes of the groundmass, the Mg being derived from the melt or concentrated from the Mg-component of the original phenocrysts. Some of the groundmass pyroxenes may also crystallize directly from the phenocrysts by solid state reactions. Occasionally where P_{H_2O} is high enough, as in confined gas cavities, the Mg-rich biotites and hornblendes form by reaction with the gases. The formation of Mg-rich biotite in cavities left by escaping magmatic gases may be illustrated by the following reactions which also have considerable interest in other petrogenic environments:



Of course the annite here must be regarded as being in mutual solid solution with $KMg_3Si_3AlO_{10}(OH)_2$ (phlogopite component). Similarly, sanadine is probably usually in mutual solid solution with an albite component, and even magnetite may dissolve $MgFe_2O_4$ (magnesioferrite) at higher temperatures. It is apparent that reactions (k) and (l) are driven to the right by increasing P_{O_2} and decreasing P_{H_2O} . The same effect is also accomplished by decreasing the total gas pressure. The right side of these reactions will also be favored by the spontaneous mixing of sanadine and magnetite in their respective solid solutions with albite and magnesioferrite.

If we consider a mineral assemblage composed of biotite, sanadine, magnetite, and hematite, the reactants and products of reactions (k) and (l), we have a system of five components³ and five phases, including the gas. According to the phase rule this system is univariant under constant temperature conditions. Under these conditions the ratio $MgO/(MgO + FeO)$ of biotite is a univariant function of the total gas pressure. Thus a gradually decreasing gas pressure in a gas cavity would be expected to favor a Mg-rich biotite as inferred from the light color of the biotites observed in these cavities.

Reaction (k) has also been studied experimentally by Wones (1958). In these experiments biotite was in equilibrium with sanadine, magnetite, and the fluid phase. The system therefore had a total of five components and four phases, giving three degrees of freedom. Consequently, if P_{H_2O} (substantially the total pressure) and T are held fixed, $MgO/(MgO + FeO)$ in biotite is a univariant function of P_{O_2} . The following relations were observed (table 2):

³ One possible choice of components according to reactions (k) and (l) is $KAlSi_3O_8$, FeO , Fe_2O_3 , H_2O , and MgO .

TABLE 2
Experimental results after D. R. Wones (1958)

T°C	P _{H₂O} psi	P _{O₂} atm	Atomic ratio Mg/(Mg + Fe ²⁺)
700	30,000	10 ⁻¹⁸	0.23
700	30,000	10 ⁻¹⁸	0.13
800	30,000	10 ⁻¹⁴	0.44
800	30,000	10 ⁻¹⁸	0.32

These results are perfectly consistent with the thermodynamic theory and the field relations as discussed.

It should be emphasized that here again, as in the case of metamorphic reactions, it will in most cases be impossible to consider oxidation independently from other effects such as hydration. It is usually only under experimental conditions that factors other than P_{O₂} can be held constant. But at times the same result may be studied by the observation in nature of selected mineral assemblages such as those involved in reactions (b) to (d).

The system MgO-FeO-Fe₂O₃-SiO₂.—Oxidative processes in magmatism are greatly elucidated by the study of analogous experimental systems. Therefore, the work of Muan and Osborn (1956) on the system MgO-FeO-Fe₂O₃-SiO₂ is worthy of special attention. This system has features in common with many natural systems. For example, the coexistence of two to three crystalline phases exhibiting extensive solid solubility between Mg and Fe²⁺ end members is characteristic of this important subsystem of petrogeny. These solid solutions coexist with the liquid over a wide range of temperatures and partial pressure of oxygen, and this effectively restricts the total number of solid phases which occur in the system. Thus the changing conditions of T and P_{O₂} are frequently reflected in changes in composition of the phases already present rather than in the disappearance of certain phases and the appearance of new ones.

Muan and Osborn have discussed three idealized types of crystallization. Only two of these types need concern us here; they are as follows:

- I. The total composition of the condensed phases remains constant.
- II. P_{O₂} remains constant but the total composition of the condensed phases may change.

Condition I is approximated in closed systems when the volume of the gas phase is small. The situation is then analogous to that prevailing in classical phase equilibria studies in nonoxidative systems. Condition II is achieved when the volume of the gas phase is large or when the reacting system is connected to a reservoir of gas of fixed composition.

During strong fractional crystallization under condition I, liquids that begin to crystallize in the primary phase volumes of olivine, pyroxene, magnesioferrite, or silica move toward and eventually reach quaternary univariant lines along which these liquids become enriched in Fe²⁺ and total Fe as crystalliza-

tion proceeds. Along these univariant lines there is a steady decrease in the ratio $\text{MgO}/(\text{MgO} + \text{FeO})$ and $\text{Fe}_2\text{O}_3/\text{FeO}$. These same ratios of the contemporaneously separating crystals of olivine, pyroxene, and magnesioferrite undergo corresponding changes. The decrease of these ratios during crystallization is also correlated with a steady drop in P_{O_2} . Thus the general picture of liquidus crystallization in the system $\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ is closely analogous to that in metamorphic rocks and more complex systems of consolidating lavas.

Under condition II, when P_{O_2} is constant during crystallization, the liquids cannot move down the quaternary univariant crystallization paths as discussed above but are confined to the isobaric surface. These liquids tend to become enriched in SiO_2 relative to all other constituents. Under these conditions there is comparatively little change in the ratios $\text{MgO}/(\text{MgO} + \text{FeO})$ and $\text{FeO}/\text{Fe}_2\text{O}_3$ of the liquids or contemporaneously separating crystals.

Oxidation in magmatic differentiation.—Recently Osborn (1959) presented an interesting hypothesis which relates possible differentiation paths in a basaltic magma to different values of P_{O_2} . His reasoning is by analogy with the system $\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ as discussed above.

According to Osborn, the types of crystallization in conditions I and II have their counterparts in magmas. Type I crystallization, in which the total composition of the condensed phases remains essentially constant, is thought to be represented by differentiates of nonorogenic zones, and especially the Skaergaard complex, whereas type II crystallization, in which P_{O_2} remains essentially constant, is thought to be represented by the calc-alkali-series of rocks of orogenic zones, and more specifically by the basalt-andesite-dacite-rhyolite series of the Cascade Mountains of Washington and Oregon. All possible gradations between the two types of crystallization conditions would, of course, be possible.

The basis for Osborn's hypothesis lies in the following facts: Fractional crystallization of type I leads in the experimental system to an iron-rich differentiate as it did also in the differentiation of the Skaergaard. Fractional crystallization of type II leads to an iron-poor, silica-rich differentiate in the experimental system. The latter two features are of course also characteristic of the calc-alkali series. Other evidence adduced by Osborn is in the form of similarities shown by subtraction diagrams of the experimental system and those derived from the rocks. In these arguments most of the emphasis is placed on changes in the percentage compositions of oxides and on the ratio $(\text{FeO} + \text{Fe}_2\text{O}_3)/(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MgO})$.

Attention has already been called to the fact that in the system $\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ liquids undergoing type I differentiation not only become rich in total iron but also show a marked decrease in the ratios $\text{Fe}_2\text{O}_3/\text{FeO}$ and $\text{MgO}/(\text{MgO} + \text{FeO})$. $\text{MgO}/(\text{MgO} + \text{FeO})$ of the associated crystals of olivine, pyroxene, and magnesioferrite also changes in harmony with the liquid. This ratio in the crystals may, however, be quite independent of the early history of a magma series, as we have seen in the case of the San Juan lavas. The same may be true of the ratio $\text{Fe}_2\text{O}_3/\text{FeO}$ in both the crystals and the total rock. Thus $\text{MgO}/(\text{MgO} + \text{FeO})$ in crystals may reflect P_{O_2} conditions during

late stages of consolidation irrespective of previous P_{O_2} conditions during differentiation, as reflected in the ratio $(FeO + Fe_2O_3)/(FeO + Fe_2O_3 + MgO)$ of the rocks. For example, although the latter ratio may remain constant in an extruding magma, most of the iron of the ferromagnesian silicates might be converted to magnetite or hematite. Thus the ratio $(FeO + Fe_2O_3)/(FeO + Fe_2O_3 + MgO)$ is apt to reflect major differentiation trends more faithfully than the former. The latter are relatively better indicators of P_{O_2} conditions during late stages of consolidation of any given rock specimen.

It cannot be denied that the mechanism proposed by Osborn is operative in petrogenesis. Since, however, other crystallization trends may also lead to silica-rich differentiates, some idea of the quantitative contribution of Osborn's mechanism is desirable.

It seems intuitively obvious that, to at least a first approximation, the influence of a subsystem such as $MgO-FeO-Fe_2O_3-SiO_2$ upon a complex magma is less than either of the ratios $MgO/(MgO + FeO)$ and Fe_2O_3/FeO . However, the former must be in some proportion to the quantity of the subsystem contained in the magma. Figure 5 is a plot of some important relations of the system $MgO-FeO-Fe_2O_3-SiO_2$ and a rock series presented for comparison (figures 9 and 11 of Osborn). From figure 5 it is seen that in the example of the experimental system chosen by Osborn for comparison with the rock series the ratio $(FeO + Fe_2O_3)/(FeO + Fe_2O_3 + MgO)$ corresponds to range andesite-dacite. From the rock analyses (Osborn, 1959) we see that the experimental system is

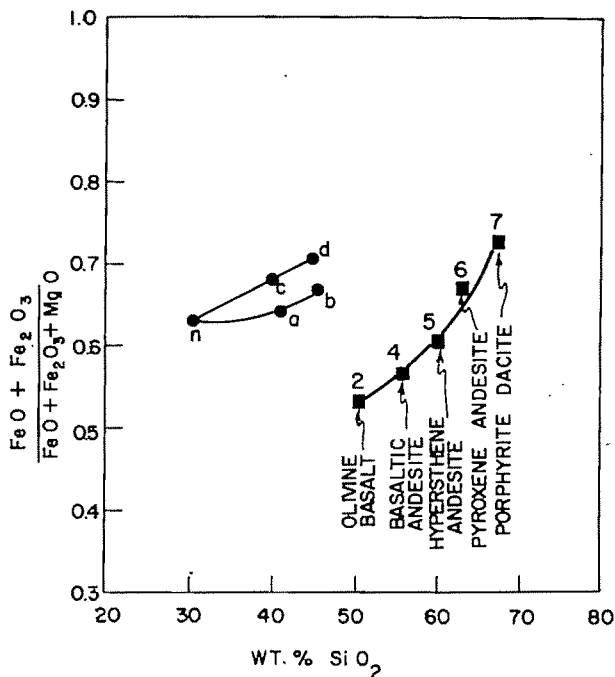


Fig. 5. Comparison of the experimental system $MgO-FeO-Fe_2O_3-SiO_2$ with Cascade volcanics which have been interpreted as a differentiation series. This figure is a composite of figures 9 and 11 of Osborn (1959).

contained in these rocks to the extent of roughly 15 percent during the differentiation interval n-c-d (fig. 5). The question then arises: Is this quantity sufficient to account for the approximately 4.5 percent rise in SiO_2 observed in the differentiation series 6-7 for this range? For the experimental crystallization path n-c-d (constant $P_2 = 0.21$ atm.) it is seen that SiO_2 increases 14.5 percent. If we multiply this figure by 0.15, corresponding to the approximate quantity of experimental subsystem contained in the rocks for the same range in the ratio $(\text{FeO} + \text{Fe}_2\text{O}_3)/(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MgO})$, we arrive at the conclusion that the 14.5 change in SiO_2 in the subsystem corresponds to a 2 percent change in the rocks. It is obvious that the value calculated in this manner may be brought to better agreement with the observed value by choosing a different crystallization path such as n-a-b in the subsystem. This attempt at evaluating the influence of the subsystem $\text{MgO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ in natural systems is a relatively crude approximation, but it does seem to indicate that the mechanism proposed by Osborn is capable of producing changes of the right order of magnitude in SiO_2 in complex systems. Since the influence of the subsystem is related to the extent it enters into the composition of the differentiating magma, its influence gradually diminishes during differentiation at constant P_2 . However, in differentiation under conditions of constant total composition, as in the Skaergaard, the influence of the subsystem should increase as differentiation progresses. In the case of the third Skaergaard liquid postulated by Wager and Deer, the system $\text{MgO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ comprises roughly 50 percent of the magma.

The point has been made here that the calc-alkali magma series appears to include sufficient quantities of the subsystem $\text{MgO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ to account for changes in SiO_2 on this basis alone. However, it is almost certain that in some differentiating magmas other subsystems, such as the system anorthite-albite, will also contribute heavily to the increase in SiO_2 . The effect of these other systems might in many cases dominate over the influence of the system $\text{MgO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$.

GENERAL CONCLUSIONS

It is apparent that manifestations of oxidative processes are widespread in many types of metamorphic and magmatic rocks. In some cases the oxidation reactions involved are between simple oxides or between oxide and metallic phases. Frequently, however, the reactions are very complex, involving changes in composition of complex crystals such as the ferromagnesian silicates. These silicate reactions may also be coupled to the gas phase through reactions involving other gases such as H_2O and CO_2 . In the latter case oxidation can seldom be considered separately but must be regarded as simply a contributing factor to the total reaction. When, subject to circumstances defined by the phase rule, oxidative reactions can be isolated for study, they may on occasion be referred to simpler systems for comparison.

Mineralogic response to oxidative processes takes a similar form in all rocks that contain the same or similar mineral series, notably the ferromagnesian silicates. In these minerals the ratios $\text{MgO}/(\text{MgO} + \text{FeO})$ and $\text{Fe}_2\text{O}_3/\text{FeO}$ increase with increasing P_2 . Similar and related responses are shown by

silicate melts of the system $\text{MgO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$. These principles have been applied to differentiating magmas by Osborn (1959).

From the nature of the underlying thermodynamic unity of the mineralogic reactions, it seems natural to extend the principles discussed above to any mineral assemblage that implies reaction between solid solutions and gases. Thus, for example, the sulfide and metallic solid solutions, as well as the co-existing ferromagnesian silicates of ore deposits and many meteorites, might be studied with a view of deducing from the phase relations and crystal composition quantities such as the temperature of crystallization and the composition of the gaseous phase.

Although the number and complexity of the phases in natural deposits might at first appear to make analysis impossible, this is partly illusion. The methods of thermodynamics are adequate to cope with systems of great compositional complexity if adequate data are available. Also the presence of additional components in natural systems usually requires the appearance of additional phases which limit the number of degrees of freedom of the system. It is therefore the mineral assemblages with a high ratio of phases to components that are worthy of the closest study and that are most likely to provide clues to the physico-chemical environment of crystallization.

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FEATHER-FRACTURE, AND THE MECHANICS OF ROCK-JOINTING

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ABSTRACT. Joint plane studies in the South Wales Coalfield reveal distinctive feather-like fracture patterns on the majority of shear joint surfaces. The pattern includes an axis, plumes or barbs diverging from the axis, and a border or fringe composed of two sets of intersecting fracture planes. Feather-fracture occurs most frequently on shear joint surfaces in fairly fine-grained rocks and is here described from rocks of varying lithologies, ranging in age from Devonian to Jurassic.

Recent experimental work suggests that the "cleavage fracture" of mild steel, which is characterized by the development of a herringbone pattern, is analogous to that of feather-fracture in rocks. Such "cleavage fracture" is characteristic of brittle failure, produces no distortion, and requires expenditure of only small amounts of energy.

Joints displaying feather-fracture may have formed similarly. The feather patterns on shear joints indicate that the main direction of movement was normal, not parallel, to the joint plane, while areas of feather divergence may be used to locate the positions of the initial fractures that controlled subsequent joint development. From a detailed study of the areas of feather divergence, it is therefore possible to attempt a reconstruction of the actual centers of initial fracture.

INTRODUCTION

A survey of jointing in the rocks of the South Wales Coalfield revealed that large numbers of joint planes have plumose or feathery markings on their surfaces. The abundance and consistency of the markings enabled a detailed study to be made, the results of which contribute new information regarding the mechanics of rock-jointing. To describe the markings, the term *feather-fracture*¹ has been adopted. It was first used by Woodworth (1896), who described similar structures in a series of Cambrian slates at Mystic River Quarry, Massachusetts. However, subsequent work on feather-fracture has been of a limited scope. The object of the present investigation is to review Woodworth's findings, to extend the study over a greater variation of rock type, and, if possible, to attempt an explanation of feather-fracture. The investigation has been carried out in rocks ranging in age from (Devonian) Old Red Sandstone to (Jurassic) Lower Lias.

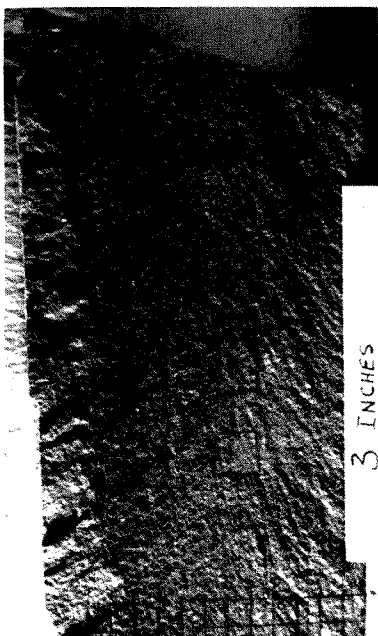
MORPHOLOGY OF FEATHER MARKINGS

The Feather

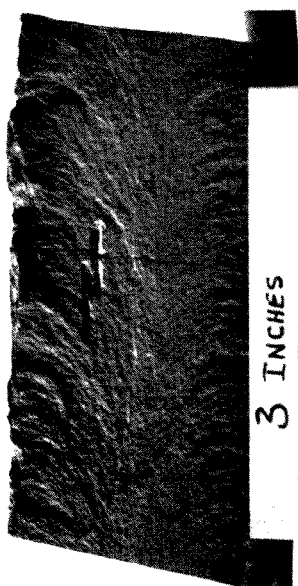
A detailed examination of almost any joint plane (pl. 1-A) reveals the following: "Even those which approach perfect planes exhibit rugosities to the eye or touch which vary from a complete series of systemless granulations of the surface to smooth regular lines, and finally a system of minor planes" (Woodworth, 1896). The phenomenon of feather-fracture alluded to in the above quotation is a delicate tracery of plumose markings on a joint surface.

¹ This term should not be confused with the "feather-joint" of Cloos which is a tensional phenomenon associated with active shear along a surface.

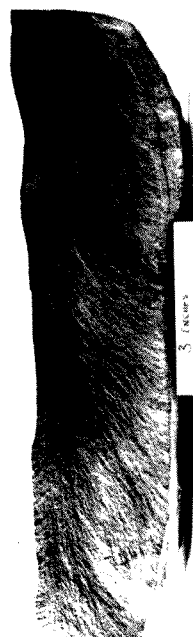
PLATE 1



B. Simple feather-fracture in flagstone.



A. Simple feather-fracture in siltstone.



C. Complex feather-fracture in flagstone.



D. Fringe showing B-planes (dark areas) and C-planes (light areas) in flagstone.

The plumes diverge from a well-defined central axis and, in the outermost parts of the fracture, pass into a system of minor planes.

The Plume or Barb

As stated above, the plume or barb is that portion of the feather that diverges from the axis as a system of well-defined lines (fig. 1). The lines are composed of a series of ridges and hollows lying in the joint surface. The surface of the joint is always hackly, never polished or slickensided, and under magnification appears to possess a granulated texture. The last characteristic is the fundamental criterion of feather-fracture and is observed on surfaces that have not undergone relative movement. The ridges and hollows of the plume are closely spaced at intervals of 0.25 to 0.50 mm. The angle which the barbs make with the axis of the feather is constant at 40 to 45°, but on approaching the axis the angle may decrease to 30 to 35°, while for a narrow sector at the joint fringe the plume passes into a C plane which dips at 70 to 75° to the axis. The direction of plume trend is constant for adjacent joint surfaces but varies considerably along the length of the joint and over the joint block as a whole; the significance of this variation is described below.

The Axis

An important feature of feather-fracture is a well-defined axial zone, whose situation on a joint block can be quite variable but is most commonly parallel to a surface of stratification (fig. 1). It has proved convenient to express plume axial measurements in terms of joint-face units. This refers to any section of a bedded unit exposed by a joint plane. For example, in several exposures of joint faces in interbedded sandstones and shales, each bedded unit had its own feather pattern, the axes of which were located and determined by some physical property within the particular unit. The control of bedding on axial distribution is very marked, and, even where folding has occurred, the axis still remains parallel to the bedding plane. The actual position of the feather axis in any one unit is variable: sometimes it occupies a median position (pl. 1-A), but more commonly it is offset towards either the upper or lower parts of the unit (pl. 1-B and C). Several axes may occur in one bedded unit, but the average is one or two per unit. The writer's observations confirm those of Woodworth that in thickly bedded rocks axial distribution is random and the axes are more sinuous.

The Border or Fringe

At the extremities of the bedded units a structure called the fringe often occurs (fig. 1). Within the fringe well-defined structural elements can be identified, which are classified as follows:

Border or B-planes (fig. 1 and pl. 1-D).—These planes intersect the joint face at angles of 20 to 25 degrees. The frequency of B-plane development is quite constant for a given block but varies with lithology, the largest B-planes occurring in the thickly bedded Carboniferous Pennant Sandstone and Devonian Upper Old Red Sandstone grits. Sometimes a well-developed shoulder forms at the fringe, which causes the B and C-planes to lie at an acute angle to the joint face, but this is of limited occurrence.

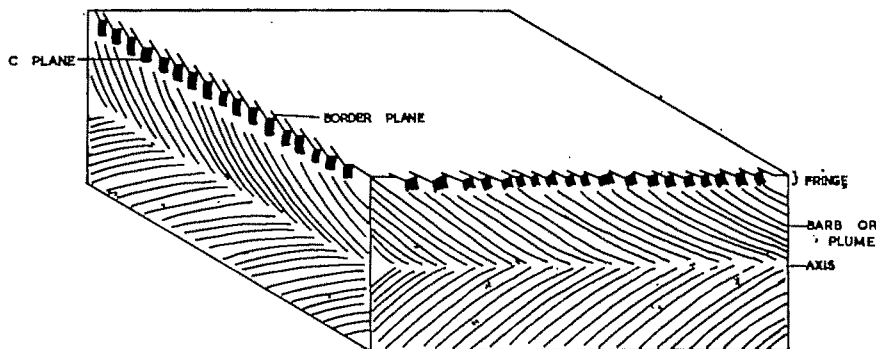


Fig. 1. Morphology of feather markings.

C-planes (fig. 1 and pl. 1-D).—These are curved cross-fractures between B-planes and the joint surface and are probably the continuation of the plume into the fringe. However, they may partly be of relatively late formation since Woodworth pointed out that, whereas feathers are frequently coated with a limonitic deposit, the C-planes are usually fresher in appearance.

The frequency of the joint-fringe itself is quite variable, feathers being far more common than fringes. Apparently the controlling factors of fringe development are (i) lithology and, (ii) thickness of bedded unit. Flaggy beds normally have well-developed fringes, while other lithologies often have completely feathered joints without an attendant fringe. Fringes occur quite commonly at the junctions of shaly and sandy beds, the fringe developing in the over- and underlying shale, the feather being confined to the sandy layer.

FIELD OCCURRENCE OF FEATHER-MARKINGS

Old Red Sandstone

Feather-fractures were studied in beds of Lower Old Red Sandstone age in a sequence of marls and sandstones along the northern rim of the South Wales Coalfield. The sandstones occur as ribs which vary in thickness from 6 inches to 3 feet and lie between shales and marls of varying thicknesses. Predominantly, feather-fractures are confined to the sandstones where they are of a simple type, but they also occur sporadically in the more blocky marl bands. The Upper Old Red Sandstone includes a thick development of grits. The grits, although current-bedded, display well-developed feather patterns of a simple character and in places show extreme development of B-planes.

Carboniferous

Carboniferous limestone.—The comparatively homogeneous nature of the rock appears to hinder the development of feather-fractures, and feathers that have developed are of a very complex variety, with sinuous axes. Of considerable interest are the spalls caused by quarrymen's blasting, which also exhibit feather-fractures, radiating outwards from the origin of the fracture.

Namurian.—It was within this portion of the succession that the majority of detailed work upon feather-fracture was carried out. The basal member of the series, a sequence of grits and conglomerates, proved unsuitable for this

kind of study. Certain thin quartzite bands display simple feathers, but the coarser grits and conglomerates (owing probably to grain-size) are entirely devoid of them. The middle member of the series, comprising a sequence of shales and sandstones, provided the ideal lithology in which to study the phenomenon. Excellent outcrops of this series in gorge sections exhibited feather variation in both horizontal and vertical directions along joint-faces. From this study it appears that the controlling factors of feather formation are (i) grain-size of the sediments and, (ii) thickness of the bedded units. The sandstones are of fairly even grain-size and almost all display feather-fractures. The nature of the bedding proved to be very important, as demonstrated by the complexity of the feather-fractures over small but discernible laminar disturbances. The effect of such disturbances causes simple feathers to diverge suddenly from their paths and to swing in a sinuous fashion over the joint face (pl. 1-C).

Lower Coal Series.—In the basal zone the tough current-bedded sandstones displayed a wide variation in feather type. Of interest also were large areas of conchoidal fracture, which have been developed by quarrymen's blasting and have acquired a characteristic feather pattern of their own. The Coal Series as a whole offers wide scope for feather-fracture investigation, the characters of which are comparable with those of the Namurian and Old Red Sandstone, the equating factor being the similar lithologies.

Pennant Sandstone.—Feather-fracture development in this series was comparatively rare. This may be accounted for by its rather coarse grain, but where feathers occur they normally attain large dimensions and usually transgress current beds, the axial trends being parallel to the major planes of stratification.

Mesozoic.—A limited investigation was also carried out in rocks of Mesozoic age and results consistent with those above were obtained. Feather-fracture in Liassic beds along the coastal areas of South Wales proved interesting since, even in the limestones, fairly simple patterns were the most frequent rule. The difference between the Avonian and Liassic limestones with regard to fracture pattern lies in their overall lithological setting. The lithology of the Liassic limestones approximates more nearly to the Namurian shale-sandstone type in having brittle layers (the limestone bands) along which feather development may occur. Border planes are of frequent occurrence at the junction of the shale and limestone layers.

POSSIBLE MODE OF ORIGIN OF FEATHER-FRACTURE

Previous work on feather-fracture has been largely descriptive. It is now proposed to present an account of the possible mechanics of feather-fracture and its relationship to jointing.

Woodworth (1896) did not give a specific account of the mode of origin of feather-fractures, and considered joints to be enlarged areas of elliptical fracture, feathers being in some way connected with them. He also states that feathers occur only upon joint surfaces that gape, separation of the joint-planes playing some fundamental part in their formation. Superficially similar structures were noted by Woodworth in media other than rock, e.g. fractured glass.

Sheldon (1912) recorded feather-fracture in her experiments on joints but did not record them in the field. She produced feathers experimentally by compressing blocks of paraffin wax in a hand vise. The blocks had to be long in comparison to their cross-section and at a low temperature. Fractures occurred which, on separation, showed no slickensides but had simple feather-like markings. She stated that . . . "the patterns consisted of a central smooth axis from which extended scales of paraffin shaped like a half crescent with the point towards the axis" and that . . . "the position of the axis of the feather depends upon the application of the pressure and the homogeneity of the material but is usually near the middle of the breaking plane" (p. 169).

Feathers were later recorded by Parker (1942), when he studied the joint patterns of the Owego and adjacent quadrangles in New York State. He found them to be well developed upon joints that he considered to be of compressional origin (shear joints), but noted their rarity upon the rough, curved joint planes that he attributed to tension.

The present writer's conclusions are in agreement with those of Parker, since he did not find feathers upon joints which are of a tensional nature. This was demonstrated during a study of joints in a small anticline, in which the joints could be grouped into three major sets. Joint sets 1 and 2 were symmetrical to the "ac" plane of the fold (at an angle of 30°), while the third set lay approximately in the "bc" plane. Joints of sets 1 and 2 were smooth faced with abundant feather-fracture and a good horizontal and vertical persistence. The latter feature, coupled with their relation to the fold-axis, suggests that the joints are the product of compressive force. The "bc" joints were short, curved, discontinuous fractures associated with normal faulting over the axis of the fold and displayed no tendency to feather-fracture.

A possible explanation of feather-fracture can be found by analogy with metal failure. However, before making comparisons a brief summary of the various kinds of fracture is appropriate.

The mode of fracture of a material depends upon a number of variables, the most important of which is the physical state of the material, e.g. brittle or ductile. Orowan (1949) has listed ten main types of fracture that depend upon the nature of the stressed material. Of especial importance to the geologist in the upper regions of the crust is the phenomenon of brittle fracture, because the rocks in this region are believed to behave as brittle solids up to the point of fracture.

Brittle materials in tension fail by brittle or cleavage fracture across a plane perpendicular to the major direction of tension (Jaeger, 1956, p. 74). Nadai (1950, p. 182) describes brittle or cleavage fracture as being of two kinds depending upon the nature of the fractured material. In amorphous materials the fracture-surface appears smooth, but if tensile stresses have been caused by a concentrated impact force, conchoidal fracture with characteristic ripples occurs. In crystalline material the fracture surface is composed of minute planes of crystallites which coincide with the surface of the fracture. Bagsar (1948, p. 770) demonstrated that cleavage fracture in mild steel has a sugary and crystalline appearance (cf. feather-fracture surface), and lacks any form of distortion and ductility.

Shear fractures occur in brittle materials in compression "along a pair of planes or a cone approximately in the direction of greatest shear stress" (Jaeger, 1956, p. 74). Most fractured rocks appear to follow these criteria which are embodied in Hartmann's Law. The characteristic of shear fracture surfaces is that they are often covered with the dust of detached particles and are sometimes polished (Nadai, 1950, p. 182). Bagsar (1948) describes shear fractures as having a silky appearance and showing evidence of deformation such as elongation and area reduction.

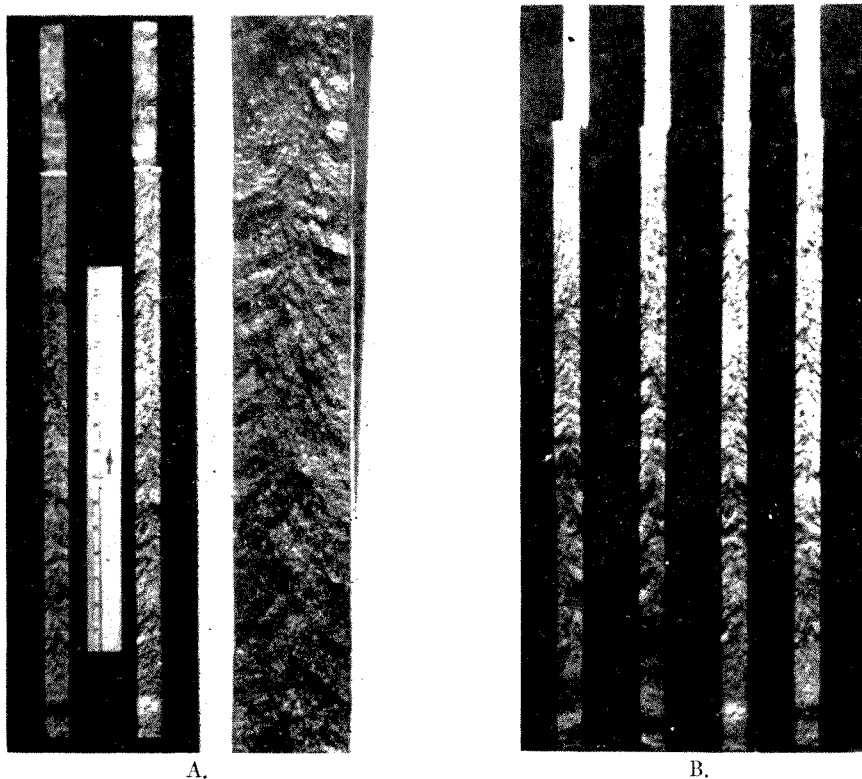
If these characteristics of fracture are applied to examples of rock fracture a number of interesting facts emerge. Joints considered due to compression and hence classed as shear joints rarely display properties in keeping with this mode of origin. If they are shear fractures in the sense of the term defined above, they should show polishing and evidence of deformation. The dearth of slickensides and general lack of evidence of horizontal movement have all been criticisms leveled against this theory of joint formation. Price (1959, p. 150) uses this to support his theory of postorogenic formation of joints, but this hypothesis fails to account for the field evidence, which often supports an early date of joint formation, prior to or concomitant with the more intense movements that accompany folding and faulting. Such movements can be shown to affect and disturb the early-formed joint sets. This is difficult to reconcile with a postorogenic age for the joint sets.

The fracture of mild steel by cleavage appears to be the key to a possible explanation of the feather-fractures observed in rocks. Nadai (1950, p. 189) cites work by Davis (1948, p. 216) upon mild steel cylinders which were subjected to high energy bursting tests. Davis subjected mild steel tubes that had been filled with oil (acting as an energy reservoir) to a strong axial compressional stress. The first fractures to form were shears inclined at 45° to the direction of stress, but as soon as the high pressure oil came into contact with the shear crack, it rapidly transformed into a cleavage fracture which displayed a characteristically "herringbone" structure.

The necessary condition for this kind of fracture is that the growing crack has access to a supply of stored energy. This experiment also indicated that the kind of fracture formed is dependent upon the rate at which the crack is forced to spread. Davis (1948) cites instances of shear fractures changing to cleavage fractures, and, upon exhaustion of the energy supply, reverting once more to shear fractures.

Bagsar (1948) investigated the nature of cleavage fracture in mild steel ships' plates. He subjected samples of mild steel to a tensile test and produced both shear and cleavage fractures. The cleavage fractures exhibited no appreciable deformation and had a lower nominal breaking strength. The surfaces of these fractures were covered by the "herringbone" pattern (pl. 2-A, B) which bears a remarkable resemblance to the feather-patterns observed upon rock joint faces (pl. 1). The "herringbone" has a well-defined axis and barbs, while the axis trends parallel to the plane of the steel plate (pl. 2). It is interesting to note that the point of origin of the cleavage fracture can be deduced, as the barbs diverge from that point. Nadai (1950) sums up brittle fracture as: " . . . one fundamental type of fracture of crystalline solids is the cleavage

PLATE 2



Typical cleavage fractures in mild steel (after Bagsar). (Reproduced by kind permission of the American Society of Mechanical Engineers.)

fracture caused by the separation of the grains of polycrystalline material along certain crystallographic planes when the tensile stress in these planes reaches a definite mean value, particularly in the lower range of temperatures and the higher rates of stressing in contrast to what is popularly called 'shear fracture' the conditions of which have been still less well observed and are little understood."

If this comparison between cleavage fracture in mild steel and feather-fracture in nature is accepted (there being a close analogy since both occur in polycrystalline aggregates of fairly random orientation), a number of speculations on possible explanations for the origin of joints may be considered. That feather-fracture is deformational in origin is supported by its widespread occurrence, its regular form and orientation throughout large areas of sedimentary rocks, and the fact that under magnification the feathers can be seen to be composed of a system of well-defined planar elements, all of which exclude the possibility of their being depositional features. The writer suggests therefore that feather-fracture is fundamental and probably the most commonly occurring form of rock fracture in the upper, brittle regions, of the crust.

The occurrence of feather-fracture on the surfaces of shear joints merits consideration, as the actual process of feather-fracture (cleavage or herringbone) is apparently a tensile phenomenon. Firstly, joints may be classified as shear joints if they can be shown to have formed in the planes of maximum shearing stress. According to the Mohr theory of fracture there is a direct relationship between the shear stress and normal stress across any plane of fracture. The observation that shear joints rarely display characteristics in keeping with true planes of shear may be explained as follows:

The formation of a joint plane requires the production of a discontinuity in a hitherto continuous medium. The discontinuity (or joint plane) is composed of two parallel surfaces, the production of which must involve separation of the medium due to a tensile stress normal to the plane of fracture. This initial fracture may form in the areas of maximum shear stress intensity, but once formed, need not propagate as true shear fracture.

The tensile forces involved in the formation of the joint plane may be of a small magnitude or absent. Bridgman (1952, p. 124) states that "The fact that fracture occurs in the actual experiment under tensions less than the hydrostatic pressure, that is, against a net compressive stress, is a consequence of the difference between the ideal and actual case. This difference is in the lateral conditions. . . . In the actual case, the sheath is not infinitely rigid, and if the external pressure is high enough, the sheath may be forced into incipient cracks, and this is an energy releasing process." Bridgman also concludes that tensile fracture of a brittle material carrying a hydrostatic stress would begin on an external surface. However, this is difficult to reconcile with the internal fracturing of a rock mass.

Therefore it is concluded that feather-fracture itself is not indicative of either shearing or tensile stress, but demonstrates that fracturing was produced by rapid separation of the medium, which proceeded with a high rate of propagation. The common occurrence of feather-fracture on the surfaces of shear joints indicates that at the time of joint formation there was access to a supply of stored energy, the medium failing by a process of internal fracturing. The relative paucity of feather-fracture on the surfaces of tectonically formed tension joints may be interpreted as follows. The process of fracturing takes place more slowly and requires the expenditure of greater amounts of energy, since the rock has to be pulled apart, thus inhibiting the formation of feather patterns. However, in the case of cooling joints, the patterns suggest that joint formation proceeded rapidly at a certain temperature, and from an analysis of the feather patterns it should be possible to deduce the location of the cooling centers.

The development of cleavage fractures in a rock under tectonic stress may originate in the following manner. Prior to actual fracture, work is continually being done upon the material. This work is probably a combination of the effects of hydrostatic loading and tectonic stress. This expended work will be stored in the material as "elastic strain energy" given by the following equation:

$$W = \frac{1}{2} \cdot \sigma^2/E$$

or for triaxial compression (Price, 1959, p. 163)

$$W = \frac{1}{2E} \left[\sigma_1^2 + \sigma_2^2 + \sigma_3^2 - \frac{2}{m} (\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_2\sigma_3) \right]$$

W = stored strain energy

σ = applied stress

m. = Poisson's ratio

E = Young's Modulus

the amounts absorbed being inversely proportional to the relative values of m and E and the difference in magnitude between the maximum and minimum stress. The values of m and E vary with lithology, and this variation has been invoked by Price (1959) to account for joint frequency in different rock types. If the compressive stress reaches a critical value at which the elastic limit is exceeded, shear fractures will form, which are symmetrically disposed to the axis of principal stress. Once the small (even incipient) shears occur, the stored elastic strain energy could be released, and the original shear fractures transform themselves into cleavage fractures. Further, the amount of strain energy expended in the formation of cleavage fractures is far less than the amount required in shear fracture, hence they have a greater tendency to spread. Therefore, the lack of slickensiding upon "shear joint" surfaces can be explained by the fact that the major direction of movement is normal, not parallel, to the joint surface. Hence Woodworth was correct in stating that the separation of the joint planes was of fundamental importance in the growth of feather-fracture, but the writer questions the implication of his observation that they were found only in "open" joints.

Scheidegger (1958, p. 98) states that "... the crack will spread if, for increasing length of the crack, the decrease in strain energy is greater than the increase in surface energy". The fractures most likely to spread are those inclined at 45° to the compressive stress, and these should propagate in their own planes. The speed at which the joints propagate is a function of the elastic energy released during their propagation, and for the joints or cracks to propagate at all, the elastic energy must be greater than the surface energy necessary to separate the two sides of the crack.

To substantiate the cleavage nature of most shear joints, and the relative ease with which they will form, the following remarks by Bagsar (1948) are particularly pertinent: "The shear or ductile fracture is less dangerous (in metals) because it is always associated with deformation which requires expenditure of a large amount of energy. Unless energy is available at the required rate to continue fracture, the extent of this type of fracture is localized. The cleavage fracture on the other hand occurs with practically no deformation and hence with no appreciable amount of energy absorption. The latter type of fracture appears suddenly as soon as a certain load level is reached, progresses with a high rate of penetration and causes more extensive damage, because only a slight amount of energy is dissipated by this type of fracturing", and, "... as stated above development of brittle fracture is favored by increasing the restraint to transverse flow, and by increasing the rate of load application." The above remarks could be equally well applied to the case of

joint formation since similar forces produce the same effects in nature, causing extensive damage to the rock mass in general.

Orowan (1949, p. 202) states that in the case of polycrystalline aggregates, brittle strength increases as grain size decreases, and from a consideration of the Inglis equation relating the stresses at the end of an elliptical hole to the length of the crack, the brittle strength of a polycrystalline aggregate is inversely proportional to the square root of the mean grain diameter. This may account for the lack of feathers in certain lithologies and may explain why rocks which are composed of a particular mean grain size (e.g. flaggy sandstone), exhibit maximum feather development. The predominance of feather patterns in sandstone is probably also related to its tensile strength, e.g. sandstone fails twice as easily in tension as does limestone (Jaeger, 1956, p. 75), and would consequently have a more rapid rate of joint plane separation, and hence a better chance of developing strong feather patterns.

The mechanism of the development of feather-fracture is probably the same as that of "herring-bone" fracture in mild steel and may be accounted for as follows: Since the divergence of the barbs of the feather indicates the point of initial fracture, then the medium must crack from the center outwards, the fracture propagating in both directions parallel to the axis of the feather. The front of the traveling crack will therefore produce a V-shaped pattern on the fracture surface.

If these conclusions regarding feather-fracture are valid, use may be made of them in accurately locating the stress centers that initiated the resultant fracture pattern. To do this the feather patterns must be traced over well-exposed joint-face bedded units, both in a horizontal and vertical direction, and the points of plume divergence along individual bedded units recorded and plotted upon a scaled block diagram. The points of divergence in each case will locate the position of the original fracture.

Thus if any one particular joint plane is examined in detail, an analysis of the points of feather divergence will demonstrate the centers from which the joint actually grew, the joint propagating outwards in both directions from a center of fracturing.

CONCLUSIONS

- (a) Feather patterns occur upon fracture surface (joints) in rocks.
- (b) The feather patterns are controlled by lithology—some rock types inhibit their development. Homogeneity and grain-size play an important part.
- (c) Feather development is apparently restricted to shear joint surfaces, since it has seldom been recorded on fractures attributed to a tectonic, tensional force.
- (d) The feather patterns are themselves a fundamental mode of rock fracture, analogous to "cleavage fracture" in steel, and can therefore be used to determine fracture centers in rock masses accurately.
- (e) The suggested "cleavage" nature of feathered joint surfaces permits a new interpretation of the mechanics of rock-jointing and explains the lack of evidence of horizontal movement along shear joints.

ACKNOWLEDGMENTS

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CLASSIFICATION OF STRUCTURES ON JOINT SURFACES

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ABSTRACT. Joint faces commonly show certain structural features such as plume-like markings and fringe joints. The description and classification of these and other peripheral or subordinate structures is useful in providing a material aid to their recognition, and is thus a necessary prerequisite to any discussion of the genesis of joints. The first detailed description and classification was presented by J. B. Woodworth in 1896. More recent study of these structures has provided additional information and makes it desirable to extend and modify this classification. The revised classification recognizes significant subdivisions of the term "joint" and treats additional structural features not discussed by Woodworth or shown in his classification. It is obvious from a consideration of the morphology of joint surface structures that any transect movement along the joint face at the time of generation of the fracture cannot occur without destroying or greatly modifying the surface structure.

INTRODUCTION

Freshly exposed joint surfaces commonly are marked with faint ridges that form plume-like or radial patterns. Associated with these primary surface structures are other subordinate or peripheral structures. Because of low relief, the structures are readily modified or destroyed by weathering agents, and the joint face then appears as a smooth, featureless, planar or curved surface. For this reason specific descriptions of such structures are rare in the geologic literature (Woodworth, 1895, 1896; Dale and Gregory, 1911; Sheldon, 1912; Parker, 1942; Raggatt, 1954; Hodgson, 1961). Recognition of joint surface structures is necessary before their genetic implications can be understood. An adequate working classification, therefore, is highly desirable.

The first detailed description of the structures on joint surfaces was published as a short note by Woodworth in 1895. This was followed in 1896 (Woodworth) by a major paper giving more complete descriptions and a classification of the structures. This work, appearing in *Proceedings of the Boston Society of Natural History*, regrettably never obtained wide circulation among geologists, and that portion concerning joint surface structures is reviewed here in some detail. Recent work (Hodgson, 1961, p. 19-23) has provided additional information on this subject making it possible to extend and modify Woodworth's classification. The purpose of this paper is to call attention to the nature of structures on joint surfaces and to present a working classification based on the more complete observations presently available.

WOODWORTH CLASSIFICATION

Woodworth's classification is based primarily on his observations of closely spaced parallel joints in argillites of the Mystic River quarries near Cambridge, Massachusetts. The majority of the surfaces examined in detail were of small size rarely exceeding 200 mm in length and were generally elliptical in shape, being elongate parallel to the bedding. On the basis of these observations Woodworth divides the joint surface into three major structural parts: (1) the joint plane, (2) the joint fringe, and (3) rim of conchoidal fracture.

Joint plane.—The joint plane commonly shows a rough, granular surface on which appear faint ridges or rays that diverge outward from a central axis or point of minimal relief and form a plume-like or radial pattern. Woodworth (1895) describes the structure of the joint plane as follows: "These apparent rays are simply cross fractures between thin laminae of rocks formed by minute planes of fracture, and some of the typical joint-planes are made up of combinations of these small joint-planes and the cross fractures." Slight variations in the size of these small joint planes and cross fractures produce the faint ridges mentioned above.

The most common structure observed is the plume or "feather fracture" which consists of a central axis from either end of which the faint ridges diverge outward toward the edge of the joint plane. Generally, but not invariably, the pattern becomes increasingly distinct and coarse toward the edge of the joint plane. Woodworth notes one example of plumose structure where two plumes occur on a single joint face and where the axes of the plumes are roughly parallel in the plane of the joint. He states (1896, p. 168): "In this case the plumose lines of the proximal sides of the splitting figures traverse the intermediate area at an angle of about 45° to the adjacent axes"

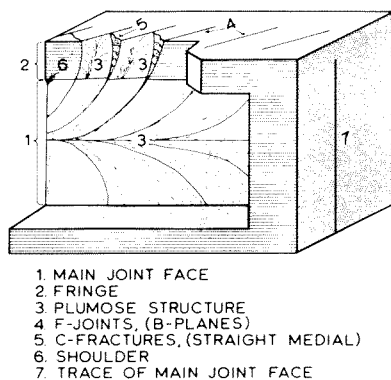


Fig. 1. Schematic block diagram showing primary surface structures of a systematic joint.

The plume is by far the most common surface structure observed on the joint plane, but Woodworth describes groups of small "discoid" joints on the surface of one of a set of large joints intruded by diabase dikes in the Mystic River quarries. The surface structure of these joints is radial rather than plumose, but in other respects the joints differ from the radial joints described below both in their rim of conchoidal fracture and in their small size. Woodworth (1896, p. 175) describes them as follows: "At a number of localities in the argillaceous strata of the Boston Basin, but nowhere more clearly shown than in the Somerville district, are small discoid fractures having a diameter varying from half an inch to two inches. The fractured surface may be divided into two fields, one forming a narrow rim surrounding the other. The large central area consists of b-planes and c-fractures, the latter radiating outwards from the center so as to expose wedge-shaped areas of the former." He con-

tinues: "The outer rim is conchoidal in its habit of fracture. The warped surface thus formed may in some specimens be likened to the rim of a soft hat curled up behind and pulled down in front. This rim of conchoidal fracture is in other cases curved upward like the edge of a saucer, so that there is a close resemblance to the ball-and-socket jointing of the prismatic columns of igneous rocks."

Fringe.—The joint plane commonly is surrounded by a fringe of small en echelon joints. Woodworth (1896, p. 169) refers to these joints as "border planes" or "b-planes" and describes them as follows: "These b-planes, where their relation to the joint plane is most clearly shown, spring out from the edge of the joint-plane with which they are at first parallel, and proceeding outward turn gradually so as to be inclined from 5 to 25 degrees or more to that plane." The intervals between the b-planes ordinarily are crossed by rough, irregular

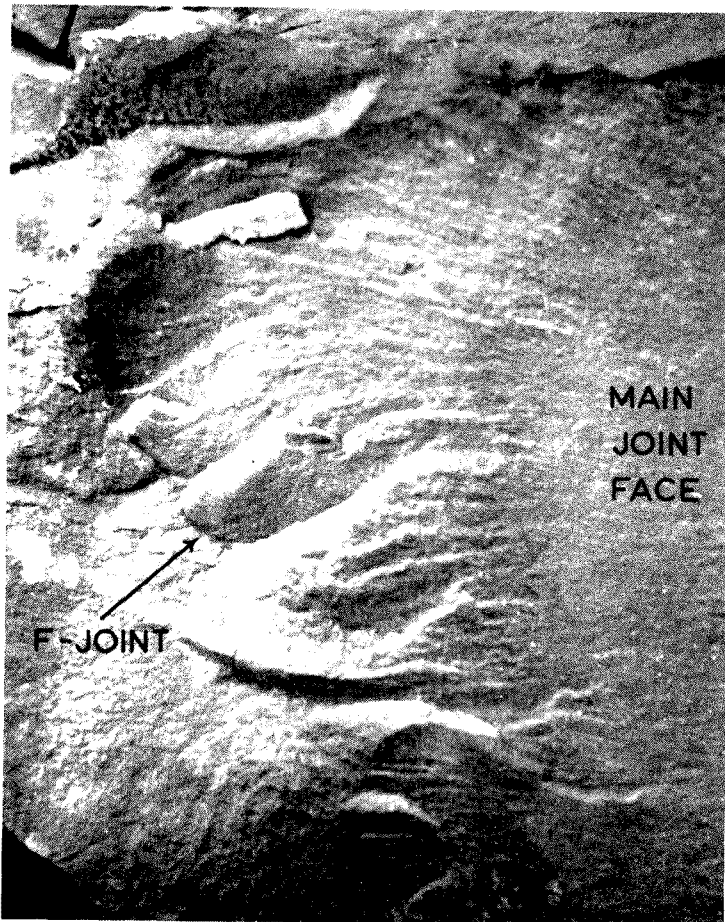


Fig. 2. Surface structures on the face of a systematic joint in a fine-grained, homogeneous sandstone of the Halgaito formation about five miles south of Mexican Hat, Utah. Note absence of shoulder and the smooth, gradual transition from main joint face to fringe joint.

fractures about at right angles to the b-planes. These are called “cross-fractures” or “c-fractures”. By far the majority of these c-fractures belong to the straight medial class (fig. 1). Woodworth notes one example, however (1896, pl. 1, fig. 2) where the c-fractures of the fringe are curved and merge into one another forming a continuous scalloped surface. These are described as “curved lateral” c-fractures.

Plumose structure is not restricted to the main joint plane but occurs also on the b-planes (see figs. 1 and 2, and Woodworth, 1896, pl. 1, fig. 9).

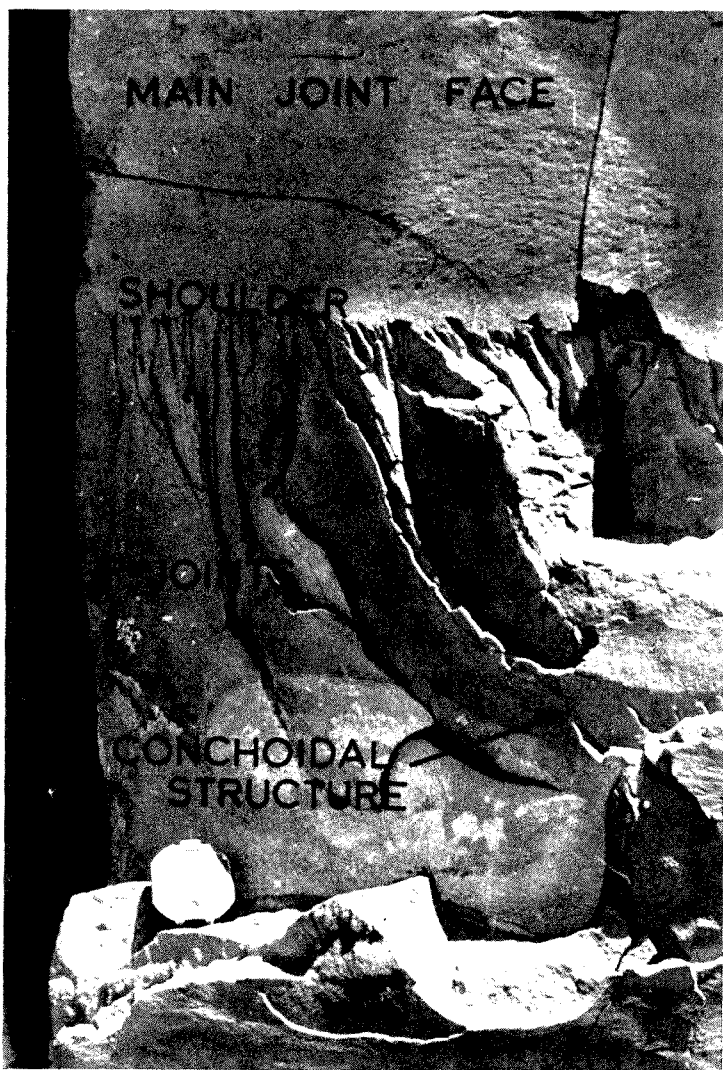


Fig. 3. Surface structures on the face of a systematic joint of great size in the De Chelly sandstone member of the Cutler formation near Oljeto, Utah. This joint is unusual in displaying a prominent shoulder and conchoidal structure associated with fringe joints.

Rim of conchoidal fracture.—Woodworth (1896, p. 173) describes the rim of conchoidal fracture as follows: “Outside of the fringe, or bordering the

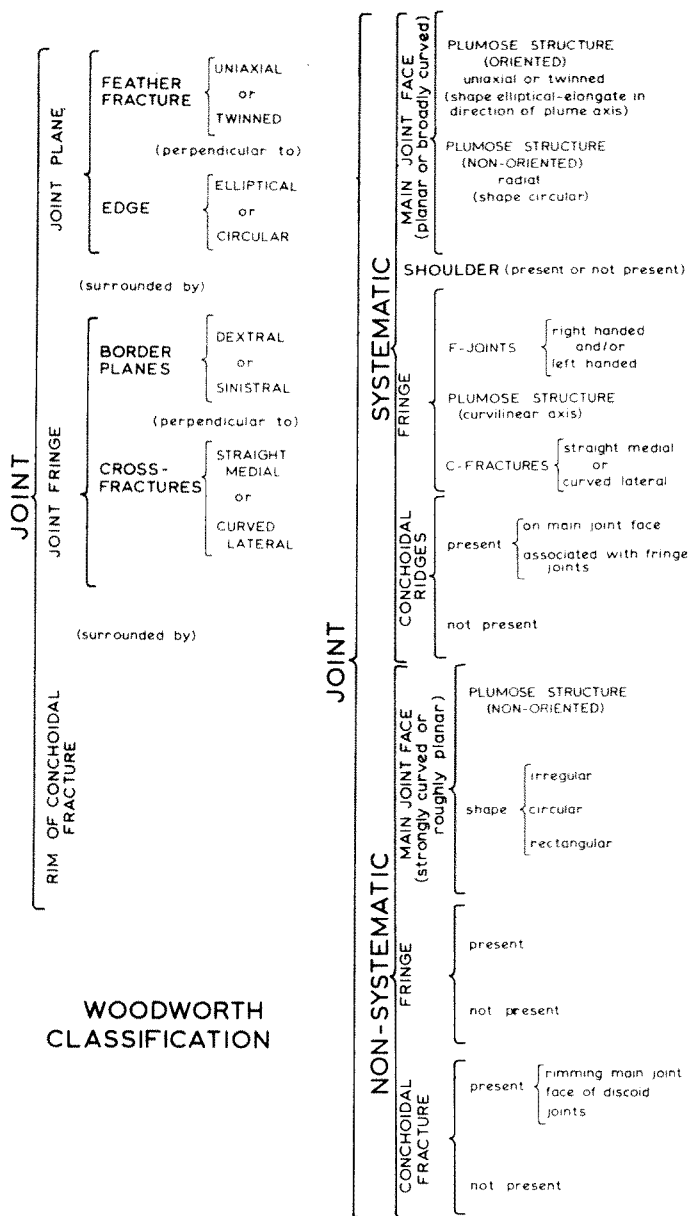


Fig. 4. Outlines of the Woodworth (1896, p. 173) and revised classifications of structures on joint faces.

joint-plane when the fringe is wanting, there may be developed a rim of conchoidal fracture. Structurally the rim is a compound surface of fracture. It tends to be inclined to the joint-plane and to the joint-fringe." The rim of conchoidal fracture as described above appears to be restricted to discoid joints.

Shoulder.—Woodworth (1896, p. 170) notes the existence of a shoulder or curved edge to some joint planes where they join the fringe. He describes the shoulder as follows: "Even when the surfaces of the fringe and the joint-plane are parallel, there is sometimes an offset or shoulder of hackly fracture, separating the two planes." This structure which is very prominent on some joints (fig. 3) is not noted in his classification.

Classification.—Figure 4 shows the classification as it appears in outline form in Woodworth (1896, p. 173).

REVISED CLASSIFICATION

Woodworth's detailed observations, although limited primarily to joint surfaces of small size, apply equally to joints of great size. All structural features tend to increase in size proportionally with increase in the size of the joint (compare figs. 5 and 6). It should be noted also that the relief of surface structures may vary from joint to joint of roughly the same size (compare figs. 3 and 6), apparently being related to the lithology of the host rock. The plumose pattern commonly has greater relief in coarse-grained than in fine-grained rocks.

The classification devised by Woodworth is perhaps oversimplified in two respects: (1) no distinction is made between major classes of joints and (2) structural features described in his paper are not included in the classification.



Fig. 5. Surface structures on the faces of systematic joints in a fine-grained sandstone of the Meriden formation near Berlin, Connecticut. Note the shoulders formed here by the abrupt transition from faint to prominent plumose structure across the boundary between joint face and fringe.

My own observations would indicate that undue prominence is given certain structural features. For example, the "rim of conchoidal fracture" might be thought to occur around the fringe or joint plane of any type of joint, whereas, in fact, it is restricted to discoid joints and therefore is a relatively minor structure.

The general term "joint" can be broken down into at least two major subdivisions based on the spatial relations and geometry of the joints (Hodgson, 1961, p. 12-13). These subdivisions are: (1) systematic joints and (2) non-systematic joints.

Systematic joints occur in sets within which the joints belonging to each set are parallel or subparallel in plan and which display the surface structures described by Woodworth (except for the rim of conchoidal fracture). In contrast, nonsystematic joints display random, curvilinear traces in plan and section and lack oriented surface structures.

Systematic Joints

The surface of a systematic joint can be divided into two major parts: (1) the main joint face and (2) the fringe. Important subordinate structures found on the faces of some systematic joints are the conchoidal ridges shown in figure 7.

Main joint face.—The main joint face may be planar or broadly curved, and plumose structure, where observed, is oriented, the axis of the plume commonly being roughly parallel to the upper and lower boundaries of the rock

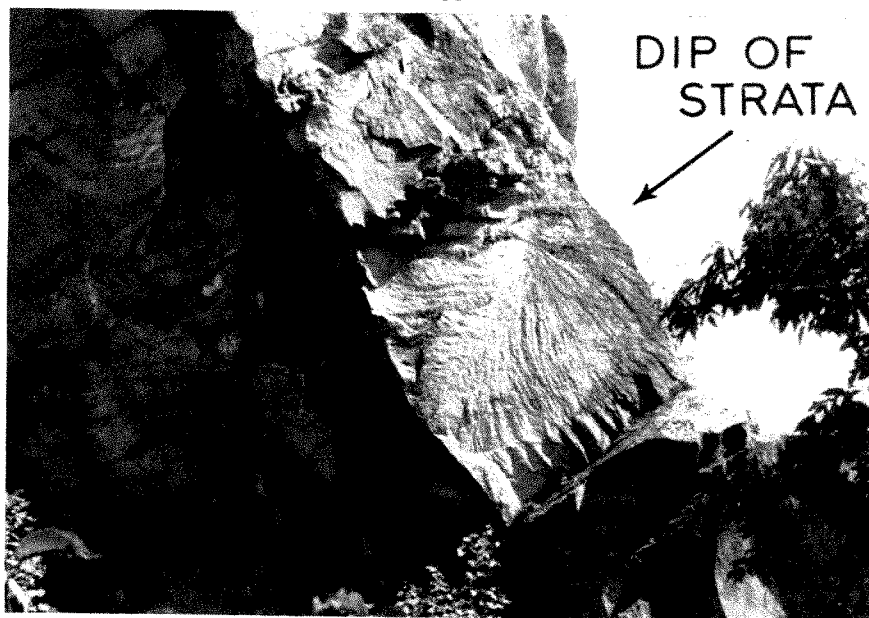


Fig. 6. Prominent surface structures on the face of a systematic joint in a massive, coarse-grained, cross-bedded sandstone of the Cloverly formation on the east flank of the Bighorn Mountains about ten miles southwest of Sheridan Wyoming. Note the relatively coarse nature of the plumose and fringe structures compared with those shown in figure 3. The joints are roughly comparable in size.

unit in which it occurs (see figs. 2 and 5). Less commonly the plume axis occurs roughly perpendicular to the boundaries of the rock unit as shown also in figure 7. Most systematic joints are elliptical in shape, ranging from very elongate to moderately elongate in the direction of the plume axis.

Rarely the surface structure on the joint face is radial, diverging outward from a point rather than an axis and producing a roughly circular joint. I have observed such radial patterns on the faces of systematic joints belonging to the same set as joints exhibiting plumose surface structures. An excellent example of a radial joint is figured by Raggatt (1954, fig. 1).

Shoulder.—In some cases the main joint face is separated from the joint fringe by a pronounced shoulder. The shoulder, where present, is formed by an abrupt curving of the main joint face at the edge (fig. 3) or by the abrupt termination of the fine ridges of the main face against the prominent en echelon joints forming the fringe (figs. 5 and 6).

Fringe.—The fringe surrounds the main joint face and is the terminal structure of the joint proper. It is composed of small joints that are set en echelon at an angle to the main face and appear to be enlarged terminal extensions of certain of the plumose ridges. The angle between the joints of the fringe and the main joint face is acute but may vary greatly from joint to joint as noted by Woodworth (compare the fringes of the joints shown in figs. 2, 3, 5, 6). The departure in strike from the main face may be accomplished gradually or abruptly (compare figs. 2 and 3).

CONCHOIDAL STRUCTURE

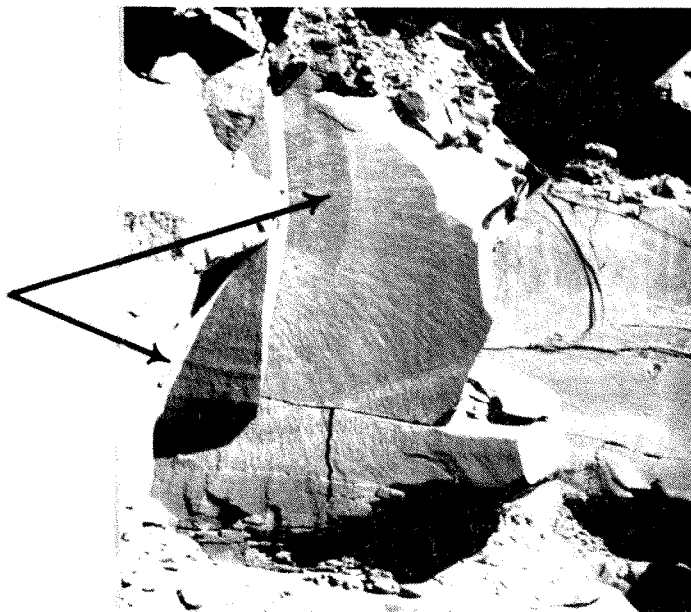


Fig. 7. Surface structures on faces of systematic joints in a fine-grained, homogeneous sandstone of the Halgaito formation about five miles south of Mexican Hat, Utah. Prominent conchoidal ridges are present on the faces of two joints marked by arrows. Note that the plumose structure on the left-hand joint is vertical, whereas it is horizontal on the other joints shown. Bedding is horizontal.

The joints of the fringe are called border planes by Woodworth and "terminal offset faces" by Hodgson (1961, p. 21). A better term would be "fringe joints" or "f-joints", denoting the occurrence and restriction of these joints to the fringe. This term is used through the remainder of the discussion and in the revised outline classification (fig. 4).

The direction of offset of the f-joints with respect to the main joint face is left-handed or right-handed and, perhaps, in both directions on any individual joint. The last condition has not been observed with certainty owing to the lack of complete exposures of the entire fringe of any single joint. The most common relations between the f-joints and the main joint face are shown diagrammatically in figure 1.

Woodworth denotes curved lateral fringe structures as a type of cross-fracture. His illustration of this structure is very clear (1896, pl. 4, fig. 2). It would appear, however, from this photograph that the fringe is composed of a series of curved f-joints that curve into one another at one edge forming a continuous scalloped fringe. True c-fractures seem to be wholly lacking and the main faces of the fractures are set en echelon and show evidence of plumose structure. Lacking additional information, however, I have retained the curved lateral designation under c-fractures in the revised classification.

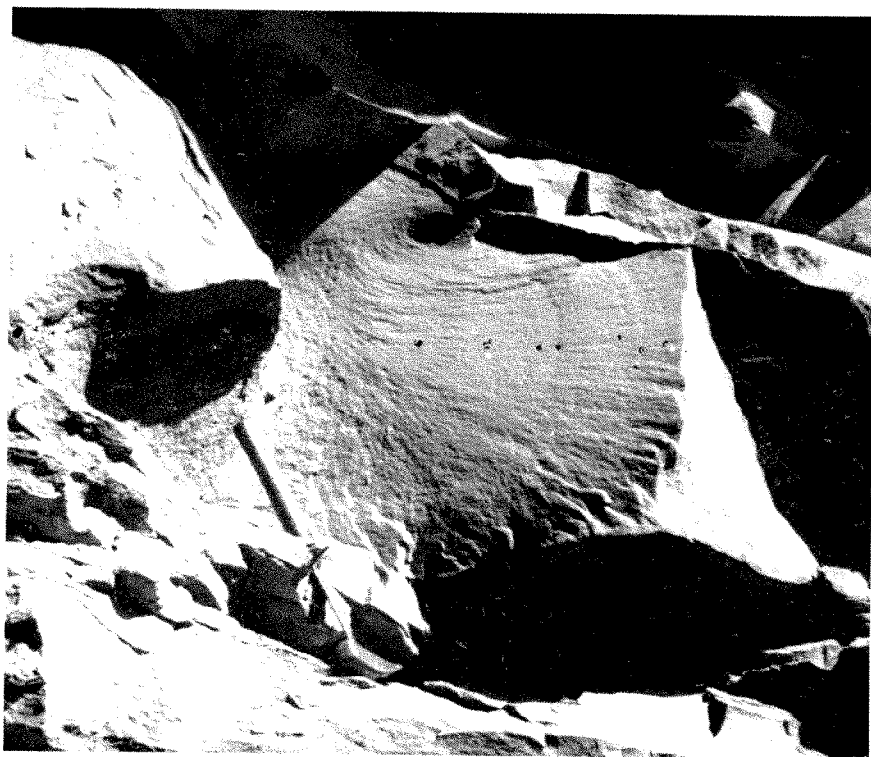


Fig. 8. Prominent plumose and fringe structure on the face of a non-systematic joint in a fine-grained, homogeneous sandstone of the Halgaito formation. Note curvilinear nature of the plumose pattern and the gradual transition from plumose to fringe structure.

Conchoidal ridges.—Conchoidal structures other than those described by Woodworth in connection with discoid joints have been described by Hodgson (1961, p. 21-22, fig. 21). The faces of some systematic joints exhibit pronounced conchoidal ridges, which have a greater relief and wider spacing than the ridges of the plumose pattern and are commonly concentric about the center of the joint face and bisected by the axis of plumose structure. Such ridges are shown on the faces of systematic joints (fig. 7). In a few examples conchoidal structure has been noted in connection with f-joints (fig. 3).

Non-Systematic Joints

The surfaces of non-systematic joints commonly are strongly warped or curved (fig. 8). The pattern of plumose ridges when present is curvilinear or irregular, lacking a well-defined axis and appearing to originate at some point near the edge of the joint. F-joints are present in some examples where one edge of the joint appears to have terminated within the rock. The fringe ordinarily is lacking, however, because many non-systematic joints terminate against other non-systematic or systematic joints.

Cross-joints (Hodgson, 1961, p. 18-19) present a particular case of non-systematic joint. They are roughly planar fractures that extend across the intervals between systematic joints of any given set. The surface of the cross-joints is rough and granular in appearance as on a systematic joint but lacks any well-defined plumose or radial pattern and also lacks the fringe inasmuch as the cross-joint characteristically terminates against some systematic joint.

Revised Classification

The revised classification (fig. 4) presents in summary form the additions to and modifications of the Woodworth Classification as based on the preceding discussion.

CONCLUSIONS

The study of the structures of joint faces leads to the certain conclusion (Woodworth, 1896, p. 166; Hodgson, 1961, p. 23) that, where these structures exist, there has been no discernible movement along the joint face at the time of formation of the joint. Such movement could not occur without destroying or greatly modifying plumose and fringe structures. The convergence of plumose and radial structures toward the center of the joint face strongly suggests that joints are fractures initiated at a point and propagated outward through the rock from that point.

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THE ROLE OF SEEPAGE MOISTURE IN SOIL FORMATION, SLOPE DEVELOPMENT, AND STREAM INITIATION

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ABSTRACT. Field study of the podsolized soils and the drainage of an escarpment of Chatsworth gritstone (upper Namurian) in Northern England has suggested hypotheses relating to stream initiation and crestral development.

Moisture moving from crests over dip slopes of less than 5° becomes concentrated in narrow lines of relatively deep soil of distinctive phase. These lines are termed "seepage lines" and form a dendritic pattern linked directly to visible drainage lines. Colluvium has gathered in certain depressions at the head of visible scarp and dip streams, and corrosion of the underlying bedrock, by accumulated seepage moisture, is taking place at depth. This corrosion of bedrock in seepage hollows is considered to be a major factor in the headward extension of first-order streams.

Moisture accumulation on crestral areas is limited so that corrosion and soil formation take place but slowly, or not at all, at least under present conditions. A crestral rock platform is thus preserved, with rock bastions or "tors" located upon it, the heights of which represent the thickness of material removed from the adjacent slopes by a combination of periglacial mass-wasting and postglacial surface and subsurface denudation.

Detailed studies of the soil mantle on such low-angle slopes on a uniform bedrock material have failed to establish any simple relationship of soil depth, profile, or texture with degree of slope or facet type. Position on the total slope in relation to the seepage net and indirectly to the drainage net is the most significant factor in soil formation and hence in slope development and denudation.

INTRODUCTION

The aspect of the form and development of slopes that has been most intensively studied is the actual surface, that is, the angles of slope units and their assemblage into complex elements or forms. This paper attempts to take into account the significance of variations of depth of soil occurring on apparently simple slopes in watershed areas, particularly in the Southern Pennines. Less-detailed studies have been made on Saale till in West Jutland and on sandstones at Leith Hill and at Crowborough in Southeast England.

A survey of podsolized soils in a recently forested area in Central Derbyshire, based on a cuesta of upper Namurian sandstone, shows that downwearing of backslopes and the extension of the drainage net into watershed areas can take place rapidly, even though the streams on massive Carboniferous sandstones are widely spaced and the drainage density is low (Strahler, 1957, p. 916).

The field data and observations concern (i) bedrock rotting by seeping moisture in deep layers of loose sand that rest in shallow depressions upslope from the perennial sources of first-order streams (figs. 2, 3, 4); (ii) direction of seepage along narrow lines from crestral areas over smooth slopes of 1° to 5° towards integrated drainage channels on the surface (figs. 1, 5). Such seepage lines are reflected in local overdeepenings of the solum on the slopes. These lines of overdeepened soil are directly connected to visible lines of drainage, though they have no appreciable surface expression except for being wetter than their surroundings during winter months. Soil profiles within two colluvium-filled depressions and within seepage lines prove dominantly vertical seepage within the solum and onto the underlying rock. This differential in the

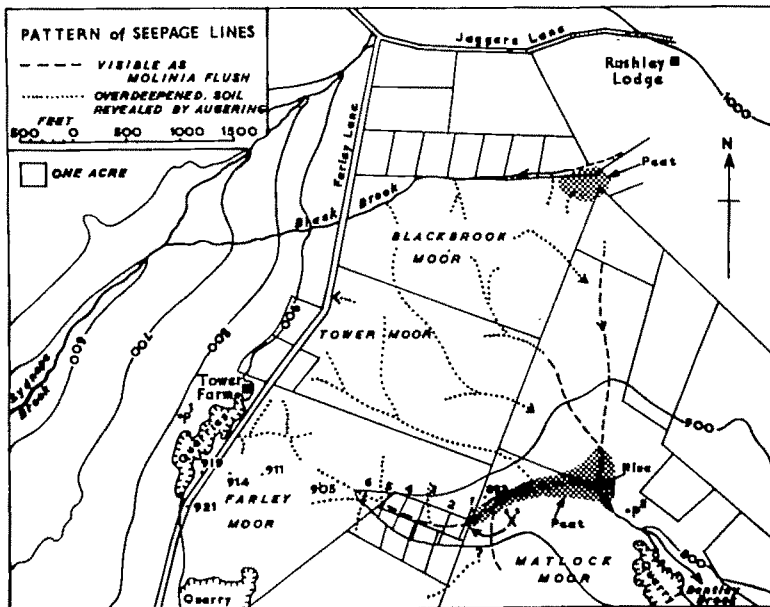


Fig. 1. Location and trend of seepage lines and hollows, Farley Moor. Integrated drainage in first and second-order streams is shown by continuous lines, P¹ and P² are the end points of the section along the opposing seepage lines in figure 4.

depth of soil formation could be considered an essential preliminary to the formation of surface gullies and rills and to the headward extension of first-order streams.

LOCATION

The area first examined comprises about 370 acres of moorland known as Matlock Moor, Farley Moor, Tower Moor and Blackbrook Moor (fig. 1). It is mainly covered by *Calluna* heath, though part of Matlock Moor was reclaimed for pasture eight years ago.

The form of the land is typical of much of Northern England. A gritstone layer, the Chatsworth Grit, lies in a shallow, southeastward-pitching syncline and forms scarps facing west, northwest, and northeast—this last forms the western rim of the Ashover pericline. The Chatsworth Grit dips 4° from the crestal areas toward the perennial source of Bentley Brook, which rises at a height of 856 feet in a bed of peat resting on the grit. To the southeast Bentley Brook has cut down through the Chatsworth Grit into the underlying shales to form Lumsdale, which is underlain by the Kinderscout Grit.¹

A grid survey of soil augerings at 200-foot, 50-foot, and occasionally at 20-foot intervals, supplemented by the digging of pits and trenches (16 to 48 inches deep) showed that the generally shallow podsolized soils of such moorland were varied by two areas of relatively very deep soil, the one close to Farley Lane, the other in the northeast corner of Farley Moor. Profiles in the latter area shed much light on the process of bedrock rotting and on the mechanism of headward extension of first-order drainage lines close to crests.

¹ Ordnance Survey, 1:63,360 map, 7th edition, sheet 111 (Buxton and Matlock), grid ref: SK/3063.

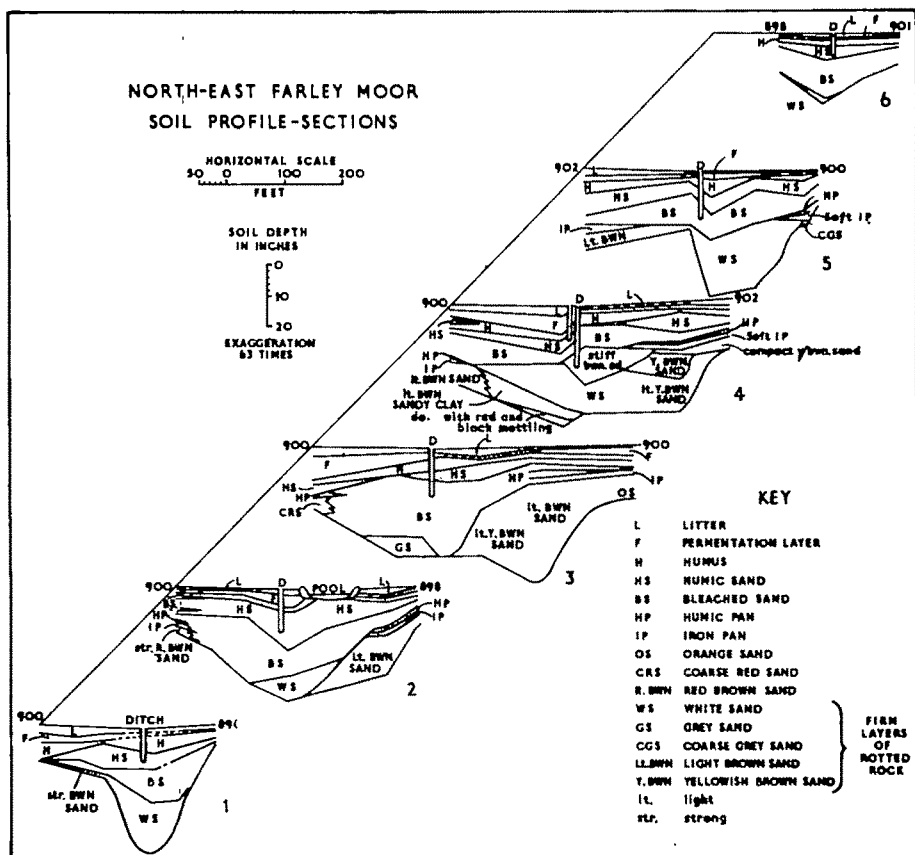


Fig. 2. Lateral sections of the seepage hollow in the northeastern part of Farley Moor. (See fig. 1 for the trend of the sections.)

BEDROCK CORROSION BY SEEPAGE MOISTURE ACCUMULATION

The extent of this eastern seepage hollow is 1000 feet in length, 200 feet wide in its broadest part, and it is not connected directly to the stream source but has a restricted outlet on its downslope side represented by a narrow line of overdeepened soil (fig. 2, section 1 and fig. 3, section X). The lowest section across the full width of the hollow (230 feet, fig. 2, section 2) shows a depth of 40 inches of loose bleached sand (10YR8/2)² of which 81 percent (by weight) has a particle size greater than 0.2 mm (table 1, d). The underlying layer of rotted rock is the shallowest of any part of the hollow and is restricted to the north side of the section. Section 3 shows a wider total section with soft bleached sand (10YR7/1) and a considerably greater thickness of rotted rock as a hardly penetrable compact layer of yellowish brown (10YR6/4), loamy sand. The three profiles clearly reflect predominantly lateral sub-surface seepage in the downslope part of the hollow changing to rapid quasi-vertical movement of moisture in the solum largely devoid of fine material at

² Munsell notation. All colors refer to the moist state.

TABLE 1

Particle size analyses of surface materials and of bedrock from Farley Moor

	Coarse sand 2.0-0.6	Medium sand 0.6-0.2	Fine sand 0.2-0.06	Coarse silt 0.06- 0.02	Medium silt 0.02- 0.006	Fine silt 0.006- 0.002	Clay <0.002	Humus content % dry weight
Mineral particles in percent of humus-free soil (size in mm).								
a. Humic sand in seepage hollow	2.08	60.02	14.27	17.75	1.54	3.74	0.64	2.48
b. Humic sand on adjacent graded slope	1.76	46.22	28.31	12.75	3.96	5.93	1.25	4.38
c. Bedrock	0.49	70.50	17.16	11.34	0.44	0.54	0.0	0.0
d. Loose bleached sand in seepage hollow	3.33	77.69	10.31	7.56	0.61	0.47	0.08	0.12

the outlet (table 1, d). These deductions, based largely on consideration of the profile morphology, are also substantiated by tentative attempts to trace the movement of water by using dyestuffs in the manner described by Tamm and Troedsson (1957). The fourth and fifth sections (fig. 2) show a narrowing of the hollow and a slightly shallower solum in which seepage is dominantly vertical and slow. Greater depths of humic material are present at the surface, the upper layers are more clearly differentiated, and the layers of bleached sand are more deeply stained by humus. Particle-size analysis showed the humic sand at 10 to 14 inches to be a silty sand (6 percent of particles <0.02 mm) with a humus content of 2.5 percent (table 1, a). Only the uppermost 17 inches of the solum are made of incoherent material. The lower layers from 17 inches depth down to depths between 35 and 51 inches are very firm and resistant to the screw augur and are considered to be rotted rock.

Frequent determinations of soil moisture content, by electrical resistance methods at 10 to 14 inches depth in profile 5, showed that the layer of humic sand dried out markedly during the summer of 1959; but periodic determination of the height of the water table showed that it was never lower than 18 inches below the surface. Hence the whole layer of rotted rock was permanently wet, even in the unusually dry conditions of 1959* (Hough, 1957, p. 39). The determinations of soil moisture content showed that the lower part of the humic sand layer remained relatively dry (11.5 to 12.8 percent moisture content by weight) until mid-December 1959, despite heavy rainfall in October-December. Rainfall was apparently absorbed by the thick humus layer and only when this approached saturation did it yield moisture to the lower mineral layers. This moisture is highly charged with humus in contrast to that seeping into mineral layers on drier sites where humic layers are thinner and the delay in soil moisture recharge is absent.

From analyses of samples it is clear that the seepage hollow is receiving particles smaller than coarse silt from site (b) (table 1) and that the unrotted bedrock is apparently devoid of fine particles removable by mechanical means.

* According to Hough the percentage porosity of a dense silty sand is half that of loose silty sand (p. 36) and the permeability of uniform sand is 0.1 cm/sec and of silty sand 10^{-4} cm/sec.

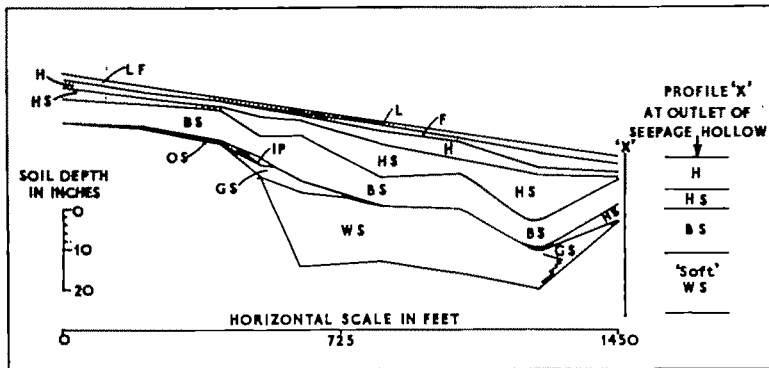


Fig. 3. Longitudinal section of the main seepage hollow on Farley Moor. (See text and fig. 2.)

The slightly more silty sand, present at depth in the upper part of the seepage hollow, adsorbs the suspended colloidal humus that seeps down from the surface. Thus humus is brought into intimate contact with the bedrock which it can corrode (Keller and Frederickson, 1952).

Upslope from this seepage hollow the very deep soils are replaced first by a narrow overdeepened profile (fig. 2, section 6) and then quite sharply by the shallow soils and thin humus layers that cover the crestal area (figs. 1 and 4). The soils on the crestal "rock platform" are rarely more than 12 inches deep, and unrotted rock lies close to the surface. The western edge of the crest is bounded by a second seepage hollow, adjacent to Farley Lane, which drains west to the scarp-foot stream, Sydnope Brook (figs. 1 and 4). Overdeepening of soil within this hollow, with soils 18 to 25 inches deep, is accompanied by marked development of surface humus and humic sand by comparison with the adjacent slopes. This represents incipient development of a scarp-face drainage line.

This first group of observations serves to show how the extension and enlargement of first-order drainage systems and valley heads take place by progressive rotting of bedrock. The so-called "headward erosion" of first-order streams takes place by selective subsurface corrosion of bedrock and removal of finer particles by subsurface as well as by surface flow. This results in the

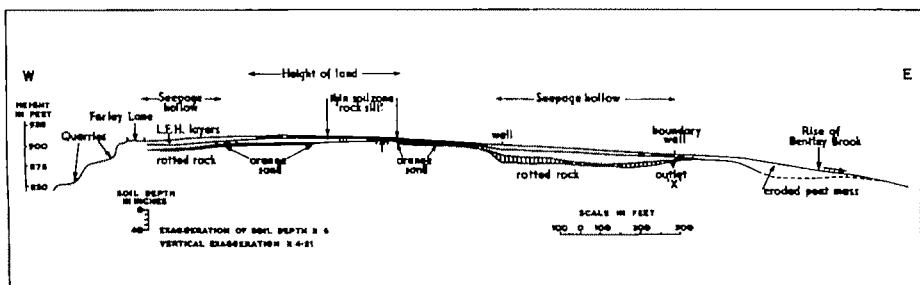


Fig. 4. Section between P^1 and P^2 (fig. 1) showing the relationship of seepage hollows to scarp and dipslope drainage. Point "T" marks the possible site of a future tor or rock platform.

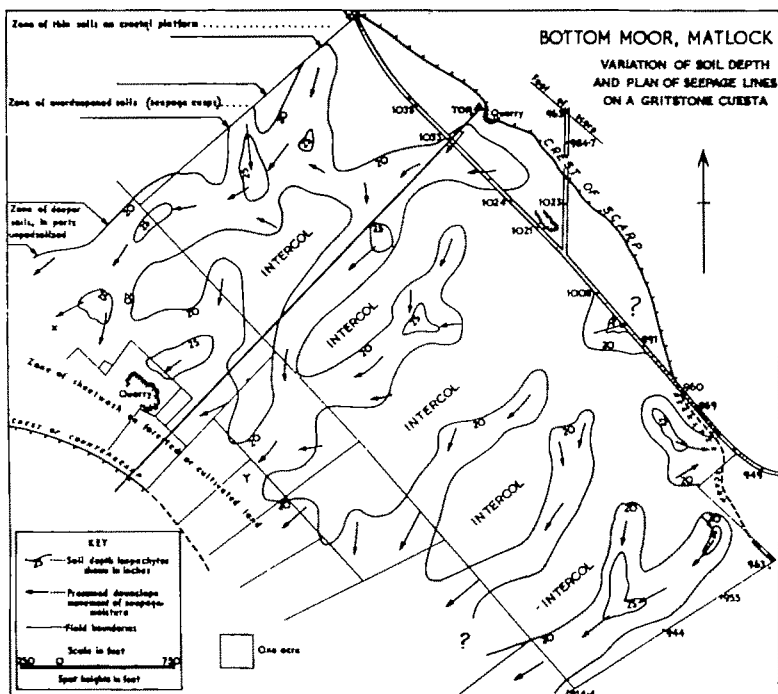


Fig. 5. Development of seepage lines and direction of moisture movement on a gritstone backslope. The tor is at the crest of the cuesta (see pl. 4) and is located closely adjacent to the longest seepage line.

stepped profile of the interface of rock and loose surface materials, the wedge of rotted rock (WS in fig. 3) being gradually softened into bleached sand and so prepared for more rapid removal in a period of increased runoff.

DRAINAGE INITIATION BY SEEPAGE LINES

A survey of Tower Moor and Blackbrook Moor revealed narrow lines of overdeepened soil, which have no coherent surface expression, trending south-eastward from near the crest at 960 feet towards the major south-trending seepage line, south of Rushley Lodge (fig. 1) visible as a line of *juncus-molinia* "flush" vegetation and possibly fault-guided.

The northwestern part of Blackbrook Moor is drained westward by the scarp stream Black Brook, which has short tributary seepage lines. Other locally overdeepened patches of soil adjacent to Farley Lane represent the beginnings of scarp drainage to Sydnop Brook. Much longer seepage lines on the eastern part of Tower Moor, i.e. on the cuesta backslope, trend south-southeast, in their uppermost parts parallel to the dip of the bedrock, though in their lower reaches directed toward the head of Bentley Brook following the slope of the land. Generally these seepage lines are much wider (ca. 200 feet) than single joint vertical planes and are unrelated to them.

A close network of augerings over the area has shown (1) significant changes of soil profile between the upper and lower parts of seepage lines; (2)

variations of profile in the areas between adjacent seepage lines directly related to the width of such areas; and (3), and most obvious, contrasts of profile as between seepage lines and the areas between them, in which case the well-known contrasts of wet and dry podsol sites are instanced. Depth of soil within seepage lines was never less than 20 inches—indeed the isopach of soil depth greater than 20 inches can be used to show such features on similar dip slopes (fig. 5)—and the maximum depth of soil recorded was 37 inches, with an average depth of 25 inches. Such depths contrast with a range of 7 to 17 inches and an average of 11 to 12 inches on the crestral “rock platform” of Tower Moor which forms the major watershed, and depths of 10 to 13 inches generally, and 16 inches at the most, between adjacent seepage lines. These areas of shallow soil between adjacent seepage lines may be termed “intercols”.

There are further important differences of profile between seepage lines and intercols. Surficial humic layers⁴ within seepage lines are everywhere more than 5 inches deep, reaching a maximum depth of 10½ inches and with the A_h layer dominant. On the crestral rock platform and on intercols humic materials are never deeper than 5 inches, though they are rarely less than 1½ inches deep and the A_t layer dominates. Humic staining of the bleached sand layer is almost absent in these latter areas, though within seepage lines the A_s layer is usually markedly stained by humus (10YR5/1) to depths, within the layer, of 7 to 16 inches. Sites with very marked humus staining (10YR3/1) are found either at the head of seepage lines or in their central parts; the latter are permanently moist close to the surface, while the former tend to dry out in summer in their surface layers (A₁ and A_t) to depths of 4 to 5 inches but to remain moist below this level. The relatively greater depth of humic staining of the mineral layer of bleached sand, wherever it occurs, is taken to represent a predominantly vertical component of seepage moisture movement; hence a more intense corrosion of bedrock can also take place.

The form and development of the iron pan (B_s layer) are also significant. The highest sites on the narrowest intercols show little or no development of iron pan. On slightly less narrow intercols the indurated layers are very thin and friable, though deposition of sesquioxides is taking place in the uppermost parts of the bedrock beneath these shallow soils (table 2, profile a). The widest relatively flat intercol areas are marked by well-developed, highly indurated thin layers of iron pan on the surface of the rock or even by layers of iron deposition within the rock, with thicknesses of up to 2 inches. Within seepage lines the B_s layer is everywhere well developed; above 2 inches thick in the shallower parts, it reaches 6 inches in the lower parts of the seepage lines but is never especially hard. The subsoil is strong brown in color (7.5YR5/8) at the head of the seepage lines, but is noticeably orange-red (5YR5/6) in the lower parts.

Two profiles are presented in table 2, to show the contrast of soil on an elevated “intercol” site and on a flat site at the head of a narrow seepage line.

Detailed descriptions of the soil profiles, as developed on various sites, have been given to show that soil phase is a reflection of denudational intensity at any one point. The greatest intensity of bedrock corrosion is apparently

⁴ The total thickness of litter, fermentation and humus layers.

TABLE 2

Soil profiles associated with intercols and seepage lines

a. Intercol site on Blackbrook Moor (south), 955 feet altitude. Vegetation: ling			b. Seepage-line site 150 feet southeast of (a), 946 feet altitude. ling, some erica and nardus		
	depth (inches)			depth (inches)	
A _o L	0-1½	Litter	A _o L	0-1	Litter
A _o F	1½-3½	Brown (10YR4/3) fibrous humus	A _o F	1-2½	Fibrous humus, nar- dus leaves dominant
A _o H	3½-5	Brown (10YR5/2) semi-fibrous dry humic mat	A _o H	2½-4	Black, amorphous, sticky humus (2.5Y2/0)
A _{1a}	5-5½	Markedly humic coarse sand, (10YR3/1) with many roots	A ₁	4-6½	Very dark humic sand (10YR3/1)
A _{1b}	5½-7	Slightly humic-stained sand (10YR5/1)	A ₂	6½-14	Dark bleached sand (10YR4/1)
A ₂	7-8½	Bleached coarse sand (10YR7/1)	B ₁	14-17½	Light olive-brown sand (2.5Y5/4)
A ₂ /C	8½-11½	Bleached medium sand with some quartz pebbles	B ₂₍₁₎	17½-18½	Iron pan (5YR4/4) lower margin in- definite
B ₁ /C	11½-12	Humic pan (10YR2/1)	B ₂	18½-20	"Orange" sandy clay (5YR5/6)
			B ₂₍₁₁₎	20-20½	Iron pan development with some black in- crustation
			C	20½-22	Brown sand (7.5YR5/2)
		At 12-12½ inches almost unaltered grit- stone with slight iron staining			At 22 inches Bedrock (10YR7/4)

achieved on sites with (1) an abundant supply of slow-moving seepage moisture giving continuous wetting of the bedrock, (2) relatively deep layers of humic material at the surface, (3) the presence of very fine particles in the deeper layers of the solum, fully capable of holding moisture and adsorbing humus (Oksbjerg, 1957, p. 264).⁵ These conditions are especially fulfilled in the upslope parts of seepage lines and hollows. In their downslope parts the texture and reddish colors of the B₂ and C horizons show that lateral eluvation of fine particles and oxidation are there taking place. Hence, apart from the headward extension of first-order streams by bedrock corrosion in seepage hollows, there is the progressive downwasting of the "belts of no erosion" (Horton, 1945) by moisture in seepage lines competent to remove material of a calibre finer than medium silt in addition to colloidal material in solution.

⁵ Concerning podsolized outwash sands in central and western Jutland, Oksbjerg makes the following interesting observation: "The leached sand is unable to adsorb the more or less colloidal humus suspensions which seep downwards from the surface humus layer. The humus material in the mineral soil is easily separated by simple mechanical treatment (shaking or blowing) of a dried soil sample". [This was far from being the case with sample b from Farley Moor (B.T.B.).] "The mineral particles of subsoil are able to adsorb humus colloids. As we do not know whether the mineral substance of the top soil is of the same origin as that of the subsoil, it may not be assumed with certainty that the leaching process itself is the sole explanation of the inability of leached sand to adsorb humus. The question is of great importance in soil science but is, as yet, insufficiently clarified."

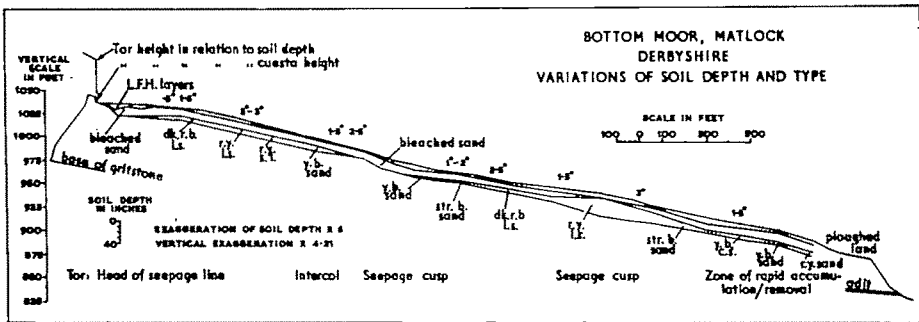


Fig. 6. The degree and form of slope in relation to soil depth and type of denudation on a gritstone backslope. (Line of section marked on fig. 5.)

Abbreviations—L.s. : loamy sand

c.s. : coarse sand

s.l. : sandy loam

dk.r.b. : dark reddish brown
(5YR3/4)

r.y. : reddish yellow

(5YR6/6 or 7/6)

y.b. : yellowish brown

(10YR5/4)

str.b. : strong brown
(7.5YR4/2)

THE OCCURRENCE AND SIGNIFICANCE OF SEEPAGE LINES

The concentration of moisture and bedrock weathering along seepage lines has been noted in several watershed areas of western Europe; for example, in Southern England, on the Lower Greensand cuesta of Leith Hill, and in Western Jutland, in podsolized soils based on till of Saale age. This latter area is known as Østerhede and Tinghede and is situated 10 kilometers south of Tarm, in the headstream area of the small second-order stream, Sønder Vium Østerbaek⁶ (fig. 7). Seepage lines are here marked by eluviated layers of thicknesses greater than 12 inches, and by thicknesses of "mor" humus greater than 6 inches, which depth increases greatly towards the point where perennial stream flow is established. The thickest development of eluviated layers of semi-indurated type (from 6 to 15 inches) occurs in the central parts of seepage lines. The nature of the "C" horizon in the lower parts of the seepage lines is a red sand, whereas a yellow loamy sand is found in the upslope parts. The variations of soil phase are therefore identical to those described for Blackbrook Moor.

That seepage lines are not exclusively phenomena associated with developed sola on gentle slopes under quasi-oceanic rainfall regimes is shown by an illustration of "a localized moist seepage with a relatively abundant growth of flowering plants in the locally more finely divided country rock" on the Bishop's Mitre, Northern Labrador (Abbe, 1938). The role of seepage moisture in establishing drainage lines and causing interfluvial downwasting is therefore clear even in recently deglaciated areas. Similarly the areas studied, both Matlock Moor and Tinghede, lie at similar distances from terminal moraines which are thought to be contemporaneous. Both areas were largely ice-free during the last glaciation, and it is possible that very similar processes of soil formation, downwasting, and slope development have held sway on dissimilar landforms during identical periods of time.

⁶ Geodætisk Institut, 1:100,000 map, 26, (Skjern), graticule ref.: 8° 28'E, 55° 49'N.

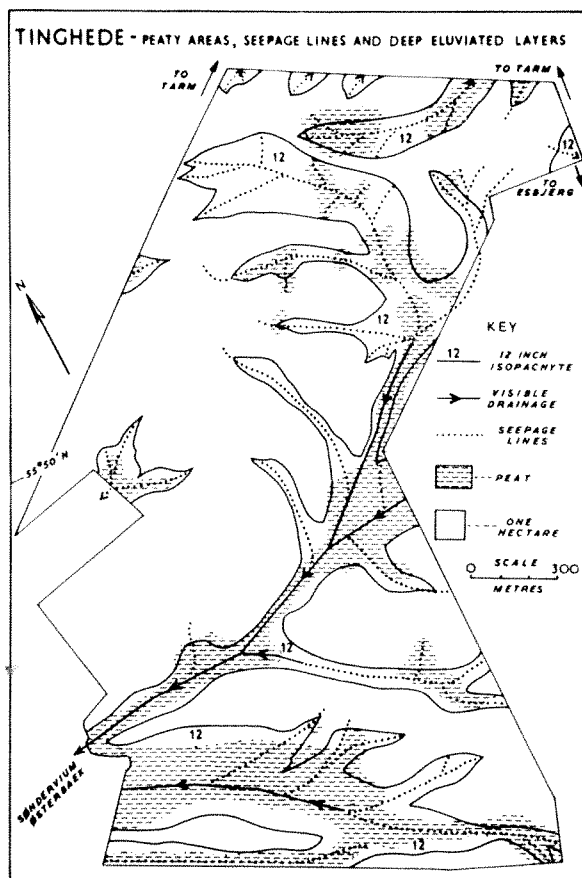


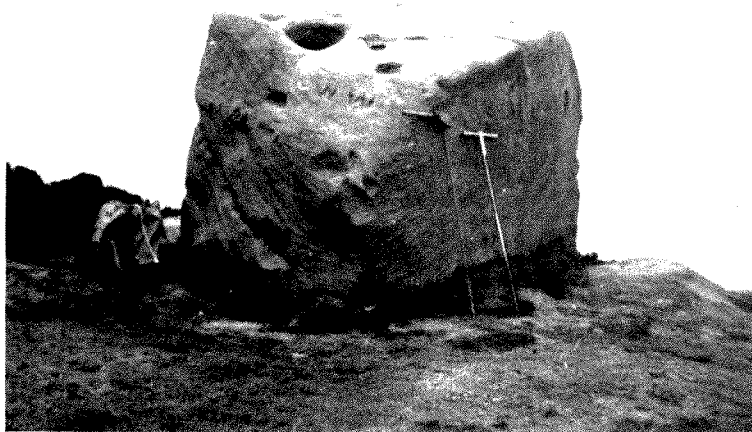
Fig. 7. Tingheide, western Jutland. The 12-inch isopach of the base of the bleached sand layer (A_2) accurately delimits lines of intensive moisture accumulation, corrosion, lateral seepage and eluviation. Appreciable surface humus and deep peat development is limited almost entirely to the seepage lines as defined by the 12-inch isopach.

CRESTAL DEVELOPMENT—THE PRESERVATION OF CRESTS AND THE DOWNWASTING OF BACKSLOPE INTERFLUVES

Many attempts have been made to assess the rate of downwasting of watershed areas and many concepts have been advanced to express the relationship of soils and the slope forms on which they are sited. Sauer is reported as stating: "The same processes that shape soils are responsible for the surface that spans the soil. . . . This most critical question, as to what happens on slopes, has received little exact attention" (Little, 1940, quoting Sauer, 1934).

To aid the elucidation of these problems, a further survey of the soil mantle of another gritstone cuesta was made adjacent to the first area and sited on the northeastern limb of the syncline at Middle and Bottom Moors, Matlock. The bedrock is the same fine-grained micaceous and ferruginous Chatsworth Grit described previously, which is not so massively bedded, coarse or compact as the other sandstones of the Millstone Grit series. The moors have an eleva-

PLATE 1



The Wire Stone, a tor of the crestal type. It has a maximum height of 8 feet but has been lowered slightly by pothole corrosion. For location see figure 5.

tion of between 1030 feet and 800 feet, the highest point being the Wire Stone, a small "tor", at 1038 feet (pl. 1). The plateau-like backslope has an average declination of 2° ; figure 6 shows that the uppermost part of the slope (1000 feet in length) is decidedly convex in form while the lower slopes provide a series of greater or smaller concavities ending in a slightly smoothed or rounded counter-scarp overlooking the Bentley Brook. The counter-scarp has been notched by two broad, shallow, dry gullies (fig. 5, x and y and pl. 2), which lead upslope to seepage lines of similar character to those described on Farley Moor, though, as the backslope in this case is broader and the distance to integrated drainage lines is greater, these are longer and more widely developed, each tending to broaden out into a very shallow "basin" (450 feet broad) of relatively overdeepened soil (fig. 5). Such areas of overdeepened soil are termed "seepage cusps" and they give the soil-rock interface a stepped profile, as can be seen in figure 6 (the general effect of the largest cusp is shown in plate 2). The broadest and deepest cusps occur at the foot of the backslope as a zone of deep (>24 inches) but generally little podsolized soils. Smaller cusps occur parallel to each other within seepage lines in the middle portion of the backslope, or else slightly "en echelon", being further upslope the more well developed the seepage line, and two or three relatively shallow "cusps" or "steps" can be contained within one major seepage line. Thus the form of the bedrock surface is slightly but significantly different from the form of the slope, or the soil surface, in a manner made readily apparent by figure 6.

The sections (figs. 3, 4, and 6) show the nature of the downwearing of slopes taking place from the base of the slope by progressive upslope migration

PLATE 2



The form of one of the shallow gullies notching the counter-scarp (X, fig. 5), representing a lowering of 8 feet. The seepage cusp upslope from the notch extends for 1000 feet as a slightly broader basin underlain by slightly-gleyed podzolic sands or else un-podzolized yellowish brown sands between 20 and 35 inches deep. Upslope from the wall on the horizon of this photograph the seepage line extends for 2000 feet but has no surface expression.

of the seepage cusp. This recalls Penck's law, "flattening of slopes always takes place from below upwards. However, it is not simply a matter of the slopes becoming flatter; but of new and ever flatter slope units perpetually appearing at the general base level of denudation, and growing at the expense of those above" (Penck, 1953, p. 138), though the slope unit in question is the soil-bedrock interface rather than the land or soil surface.

It is not known whether this process of sapping and paring by seepage cusps is initiated from a downslope or from an upslope direction. While the supply of moisture obviously comes from an upslope direction, the extension of incipient drainage or seepage lines into crestal areas must gradually cease when the crestal area, reaching some minimum width, can no longer yield sufficient moisture to the adjacent seepage hollows or cusps for the processes of corrosion to continue. Eventually, at some point lower down the seepage line, enough moisture gathers to revive the process. Periods of increased moisture collection and retention at the foot of watershed slopes lead to a more rapid corrosion of the subsurface and removal of material from the surface, at present aggravated by cultivation, while the crestal area in any case must survive, as a rock platform, with a very thin covering of soil.

Many tors are located at the apex of these platforms on cuestas of Carboniferous gritstone in the Pennines, such as the Wire Stone (pl. 1) and many others of more fanciful name (pl. 3). These tors are located either slightly downslope from the crest (fig. 4 at "T", and pl. 3), others are sited directly on

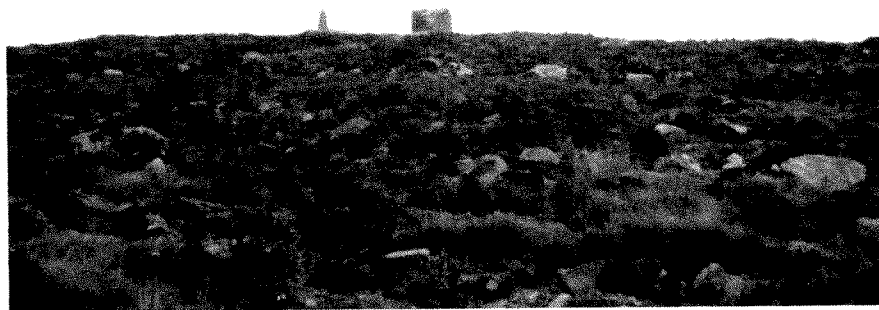
PLATE 3



The Crow Stones, Howden Moors, Yorkshire. Location SK 170971 at a height of 1660 feet. This is a tor of the first type, located away from the scarp crest, and has a maximum height of 16 feet. Two dark lines in the center of the photograph are seepage lines trending eastward (right) to the head of Stainery Clough. Movement of moisture is therefore following the hydraulic gradient to the stream head rather than to the incised portion of the stream below the scarp face (left center).

the crest so that their backslope face is much lower in height than their scarp face which merges with the free face of the cuesta (fig. 6). The Wire Stone (pls. 1 and 4) is such a tor. All the tors are completely attached to the rock that underlies the backslope. It is evident in the first type that the total height of the feature, and in the second type that the height of the free face on the backslope (pl. 4) provide a measure of the depth of bedrock removed from the backslope by long-continued downwearing by seepage moisture coupled with the possibility of occasional mass movement. Most tors are sited near minor breaches in gritstone cuestas where seepage lines are well developed and headward erosion by first-order streams is most active below the termination of the backslope. Furthermore the tors are faced on one side by steep scarps and scarp-slope seepage lines that must, in most cases, traverse block-strewn shale partings and lower layers of gritstone before reaching scarp-foot streams (pl. 3). The consequent or possibly resequent seepage or drainage lines on the backslope side of the tor are based on gently sloping plateau surfaces developed on thick beds of gritstone, which extend for some distance (200 to 2000 yards) toward deep valleys developed on the shales beneath the Chatsworth Grit, or, in north Derbyshire, beneath the Kinderscout Grit. Thus all the tors are remote from the action of integrated drainage, while the competence of moisture seepage is exhausted on the lower slopes adjacent to the tor at the base of the scarp or in seepage cusps on the backslope.

PLATE 4



This photograph of the Wire Stone gives an impression of the amount of lowering of the backslope. The tor is to the right of the survey point. The upslope termination of the seepage line is marked by the break of slope in the center of the photograph.

Preliminary calculations show that there is no correlation of tor height with the extent, slope or lithology of the gritstone bed of which it forms a part. The tor formations of Derbyshire and the West Riding of Yorkshire may therefore be regarded as minor features surmounting wide rock platforms, having been developed within a single cycle of erosion by this process of emphasizing the crestal area by the concomitant lowering of the adjacent lower slopes by seepage moisture acting on a bedrock layer identical to that which forms the tor. The tor owes its height and its survival to repeated failures of successive seepage lines and cusps to pare off the crestal rock layer.

It is possible to suggest a time which would mark the commencement of the process of emphasizing these tors. Estimates (Young, 1957, p. 149) of the rate of surface lowering of the area of a small drainage basin, 17 miles to the north of the area here examined, are equivalent to an average annual loss of a layer between 0.005 inches and 0.001 inches in thickness. The higher rate is based on determinations of reservoir sedimentation during a period of 87 years.⁷ The usual height of the Pennine tors is between 7 and 25 feet with the greater majority between 14 and 15 feet. If the tops of these features represent the central parts of rock platforms—or else of the crests between opposing seepage lines—unlowered by weathering, then their age should not be less than 36,000 years, a date which coincides with the waning of the York glacier (Flint, 1957, p. 395), nor should it be more than about 180,000 years, a date corresponding to the earlier part of the final interglacial period.

⁷ The rate of 0.005 inches per annum is the calculated lowering of the whole catchment area. The lower figure is the minimum rate from comparable areas quoted in other literature.

While the possibility exists that the tors have been isolated by removal under periglacial conditions of layers of congelifRACTate downslope from the crestal area, as has been postulated by Peltier (1950, p. 228), and an example in Alaska mentioned by Lougee: "post-Glacial mass movement of solifluction terraces has been so great that residual tower-like spines of bedrock or "tors" have been left projecting through and as much as thirty-feet about the active layer on summits and upper slopes of mountains" (in Peltier, 1950, p. 236), there is no indication of such material at the foot of the counter-scarp overlooking Bentley Brook. Granted that this may have already been removed, there is still no need to postulate a sudden removal of material by periglacial action. The greater part of the material moved to expose the tor can have been removed by: (1) the action of seepage moisture promoting subsurface rotting and later lateral leaching of fine material in the uppermost soil layers; (2) surface wash in the event of heavy rainfall or following the removal of vegetation in times past; and (3) the temporary establishment of surface flow in times of a high soil water table. Most important is that the competence of corrosion, lateral leaching, and surface flow would be greatest in wetter climatic phases when fresh material would more rapidly be exposed for colloid plucking or rotting. The calibre of particles capable of being removed on the surface varies with the annual variation of rainfall, but it is everywhere apparent that particles finer than medium silt can be removed under present-day conditions within seepage lines.⁸ This process of the selective removal of waste by seepage moisture results in the slow but continuous lowering of the soil-rock interface, even though the soil depth may remain uniform at any one place. This in the long run is a more effective process on slopes of low declivity than surface wash, creep, or other similar process of surface stripping, and it is in any case most effective towards the lower ends of slopes.

It is also evident that as the gritstone layers are pared down by the formation of seepage lines and by the action of seepage cusps, so the thickness of the sandstone layer above the underlying shale bed must be lessened (fig. 6). There comes a time when the moisture content of the layer of sandstone is always high, bedrock rotting is more intense, and eventually the headward erosion of surface water in first-order streams is much accelerated by the greater amount of water available in their catchment at or near the surface. Thus, the preparatory work of corrosion of bedrock and the removal of fine particles by seepage moisture is supplemented by movement of larger particles or masses by surface drainage either in wetter, or cooler, climatic phases, and in any case ultimately by the progressive increase of moisture content as the rock layer is thinned. Indeed, solifluction is thought possible on low-angle slopes underlain by sandstone layers, whenever the water table is high, or when the surface is so moist that movement can take place (Gullentops, 1953). Hence the crestal rock bastions, or tors, can remain unaffected until very late in the sequence of events leading to the destruction of the sandstone layer.

⁸ The removal of material in solution is also considerable. From data, supplied by Mr. S. A. Stuart (Borough Water Engineer at Matlock), concerning the silica content and yield of spring water at Palethorpe Springs, (adit, fig. 6), it is calculated that the rate of removal of colloidal silica, annually, by subsurface water, is 2187 lbs from a gritstone layer 64 feet in thickness and 300 acres in extent.

The identification of seepage lines on gentle slopes in moorland areas has practical applications. If the rate of drainage needs to be effectively increased, the seepage lines should be trenched. Since in upland areas they often debouch on improved land or hill pasture, the disposal of seepage moisture should be controlled by trenches linked directly to pipe drains. A corollary of this is that transverse trenches on such slopes are often rapidly silted up after heavy rain and pipes are rapidly filled by fine silt, clay, or ochre, even after short periods with normal rainfall, witnessing to the effectiveness of subsurface runoff and colloid plucking as erosive agents.

Establishment of tree seedlings is more certain, and their early growth appreciably quicker, in the vicinity of seepage lines. Where rapid early growth is desirable forest planting is aided by their delimitation, and obviously, too, the generally drier intercol areas are best suited for the location of forest tracks, particularly those intended for use by heavy vehicles.

ACKNOWLEDGMENTS

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PRESSURE AND TEMPERATURE OF CRYSTALLIZATION FROM ELASTIC EFFECTS AROUND SOLID INCLUSIONS IN MINERALS?

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" . . . I argue that there is no necessary connexion between the size of an object and the value of a fact, . . . "

Henry Clifton Sorby—1858

ABSTRACT. Earth processes commonly result in the transfer of a mineral grain from the pressure-temperature (P,T) condition of its origin to considerably different pressure-temperature conditions. If a mineral grain (h) includes a grain of another mineral (i), transfer to new P-T conditions commonly will cause anisotropic elastic strain effects around the inclusion owing to different coefficients of thermal expansion (α) and compressibility (β) for the two minerals. To the extent that these elastic effects remain reversible over geologic time intervals, they represent stored information concerning the pressure and temperature of origin. The differential equation for the pressure-temperature curve representing absence of anisotropic stress around an inclusion of one isometric crystal (also a homogeneous fluid) inside of another isometric crystal is:

$$\left. \frac{dT}{dP} \right|_{P_i=P_h; T_i=T_h} = \frac{\beta_h - \beta_i}{\alpha_h - \alpha_i}$$

Experimental determination of two such P-T curves (conditions: $P_i = P_h$; $T_i = T_h$) for a given host containing two different kinds of inclusions, known to have been included contemporaneously, would result in an intersection representing the pressure and temperature of origin (P_o, T_o).

Among suggested techniques for determination of P-T curves is one using a window pressure-temperature bomb for observation of specimens between crossed polarizing filters to obtain the pressure-temperature coordinates for points of null piezobirefringence around inclusions. An auxiliary method, based on conventional P-T equipment, involves an electrical null technique using either a symmetrical combination of two "slide-wire" piezometers (Bridgman) or a related device and a Wheatstone bridge. The two "slide-wires" comprise two resistances of the bridge in the first device. In the second device the bridge is unbalanced by severance of one of its arms.

The few noted natural examples of stress effects around inclusions in diamond and associated pyrope are consistent with extrapolations based on known values of α and β and inferred pressure-temperature conditions within the Earth. Examination of these minerals, having a probable origin in the mantle but now included in the kimberlites, should allow determination of specific temperatures at specific pressures equivalent to depths within the mantle of the order of 100 miles or more, using available experimental equipment.

INTRODUCTION

One principal goal of petrology is the determination of the pressures (P) and temperatures (T) of crystallization for mineral grains that have developed deep within the Earth (or in meteorites) and are now exposed at or near the surface of the Earth. Such information makes possible significant inferences concerning the character of that part of the Earth temporally and spatially inaccessible to man. To date, most of our information concerning physical conditions within the Earth's interior has been derived from relatively gross-scale geophysical observation and from comparisons of the phase assemblages resulting from physico-chemical laboratory experiments on synthetic compositional systems with the naturally occurring compositional equivalents of these systems. The chief difficulty connected with the geophysical approach has been the

multiplicity of answers that have been in accord with the available information. The chief difficulty of the physico-chemical approach has resulted from (1) lack of attainment of equilibrium in time intervals that are short relative to those during which most naturally occurring mineral assemblages probably crystallized and (2) failure to simulate the environmental conditions that led to the development of the natural assemblages.

In this paper the writers propose a new physical method for the determination of the pressure-temperature conditions for the crystallization of minerals deep within the Earth. The method is dependent upon the presence of nonopaque mineral grains that have included other mineral grains during their crystallization. In general, host and inclusion have different elastic properties. Transfer of the assemblage from the pressure and temperature of inclusion (P_0 , T_0) may result in persistent elastic strain effects in the host adjacent to the inclusion. Such effects would then represent stored information concerning the pressure-temperature conditions at the time of inclusion. The method as presently developed applies strictly to isotropic solid phases (e.g. glass) containing other isotropic solid (or liquid) phases as inclusions. Justification for extension to minerals of the isometric system is considered subsequently.¹ The extent to which minerals approximate isotropism in regard to their expansion characteristics under hydrostatic pressure governs the degree to which the proposed method will provide information concerning pressures and temperatures of crystallization.

THEORY

Basically the proposed method depends on the following considerations: First, it is probable that a mineral that grows around another mineral will do so at the same temperature (T_0) and pressure (P_0) as that of the included mineral. The included mineral (i) will furthermore be in direct contact with the host mineral (h) at all points on its surface. In the normal case, the host mineral and the included mineral will have different coefficients of thermal expansion and compressibility. Departure of the assemblage, host plus inclusion, from initial conditions, P_0 and T_0 , will, in the vast majority of the cases, result in one of two things. The included mineral will either (1) tend to draw away from its host due to *relative* shrinkage and have a lower mean pressure, or (2) it will tend to expand against its host due to relative expansion and have a higher mean pressure than that of the host. In the latter case, at least, the inclusion will tend to cause a compressive stress to develop in the host around the borders of the inclusion with maximum principal stress in the host at any point near the inclusion directed more or less radially around the inclusion.

Let the following conditions hold: (1) The host behaves as a stable elastic solid for a geologically significant period of time without creep or fracture taking place. (2) Temperature and pressure are the only external intensive factors that affect the state properties of host and inclusion. (3) There are neither phase transitions in the host or inclusion nor changes in their composi-

¹ In principle it should be possible to extend the method to combinations involving phases that are anisotropic with respect to their relevant elastic properties (e.g. minerals of relatively lower symmetry), but mathematical complexities allow only limited extension at this time.

tions. It will be worthwhile to determine a volume relationship between host and inclusion that characterizes all pressure-temperature situations for which the pressures and temperatures affecting the inclusion are equal to those affecting the host. It will also be worthwhile to determine what alterations in this volume relationship result in the inclusion having either a higher or lower mean pressure than that of the surrounding host. Further, it will be worthwhile to determine the extension of this volume relationship in a pressure-temperature diagram, as (barring creep or fracture) P_0 and T_0 must lie within such an extension.

Volume relationships for maintenance of pressure equality.—There are a number of ways of approaching the desired volume relationship for pressure equality between host and inclusion. Three ways will be described. The writers prefer the first method described below but have found the two alternate methods useful in conveying a physical picture to others. The two alternate methods are included in the section entitled: "Alternate methods for obtaining (5)." This section may be bypassed without destroying continuity.

Imagine a homogeneous isotropic solid in the interior of which there are no pressure differences (i.e. stress is homogeneous in both direction and position). Let an intensive property of this body (c) be defined in the following fashion:

$$\gamma_c \equiv \lim_{\Delta x \rightarrow 0} \frac{\Delta V_c}{\Delta x} \cdot \frac{1}{V_c} = \frac{dV_c}{dx} \frac{1}{V_c} \quad (1)$$

where

γ_c = coefficient of expansion of c with respect to x , a scalar (cf. T or P).

Δ = small change in a particular quantity in going from one value (') to another (').

V = volume.

x = an arbitrarily chosen intensive variable (e.g. temperature) that has an equal value at all points in the solid.

Consider a closed, but deformable, imaginary surface within this body across which no transfer of material is permitted. Consider the material within this

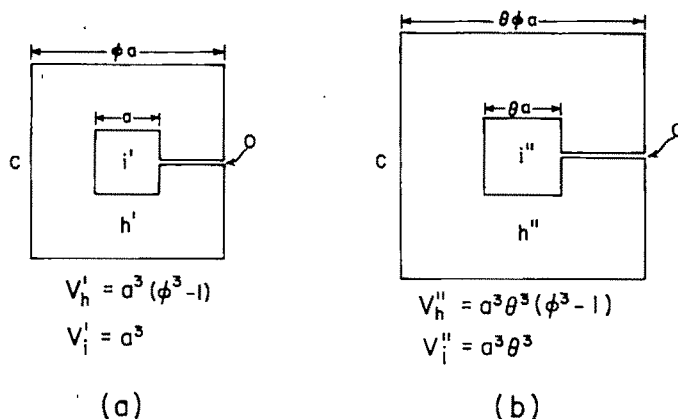


Fig. 1. Schematic diagrams to illustrate derivation of equation (5). See pages 522 and 523 for discussion. For meanings of ϕ and θ see page 523.

surface to be an inclusion (i). Let the body undergo a volume change as the result of a change in the variable x . Now, for the material of the solid outside the imaginary surface (i.e. the host, h),

$$\gamma_h = \frac{dV_h}{dx} \frac{1}{V_h} . \quad (2)$$

For the material of the inclusion,

$$\gamma_i = \frac{dV_i}{dx} \frac{1}{V_i} . \quad (3)$$

Since the whole assemblage is homogeneous and has a constant value for γ at all points,

$$\gamma_i = \gamma_h = \gamma_c . \quad (4)$$

Combining (2) and (3) in accord with (4),

$$\frac{dV_h}{V_h} = \frac{dV_i}{V_i} \text{ or } \frac{dV_h}{dV_i} = \frac{V_h}{V_i} . \quad (5)$$

Equation (5) is a desired volume relationship for the condition of pressure equality between host and inclusion. Its applicability is not affected by the substitution of some other isotropic solid for the material of i.

An additional volume relationship may be deduced from (5). Thus (5) may be restated

$$d \ln V_h - d \ln V_i = 0 \quad (6)$$

or

$$d(\ln V_h - \ln V_i) = 0 \quad (7)$$

or

$$d \ln \frac{V_h}{V_i} = 0 . \quad (8)$$

For (8) to be true, the ratio, V_h/V_i , must be constant. Therefore

$$V_h = kV_i \quad (\text{condition: } P_i = P_h) \quad (9)$$

where k is a constant. Equation (9) will be a valid relationship only if no material is added to or subtracted from the host. Also

$$dV_h = k dV_i \text{ or } \frac{dV_h}{dV_i} = k . \quad (10)$$

Equation (10) is subject to the same restrictions as (9) in regard to addition or subtraction of material.

Alternate methods for obtaining (5).—A second way of developing (5) and its consequences is to imagine a container (c) of any shape whatsoever made of a homogeneous, isotropic, solid material (fig. 1a). Let there be an infinitesimally small orifice, o (of sufficient diameter to maintain pressure equality between the inside (i) and outside of the container but of negligible volume). The container either may be filled (f) with the same material as that characterizing the container walls (h) or may contain the fluid that maintains the pressure (e). In either situation change of temperature and/or pressure will cause homogeneous expansion or contraction and will result in the same volume displacement (V_c) by the external surface of the container (c). In figure 1, (b) might represent the container shown in (a) under the changed conditions.

Let $\bar{\gamma}$ be a coefficient of fractional expansion with regard to a small change in some variable, Δx , in going from one state (') to another state (''). $\bar{\gamma}$ differs from γ of (1), as Δx has a finite value. In the limit as $\Delta x \rightarrow 0$, $\bar{\gamma} \rightarrow \gamma$. Then, for the above-described physical situation,

$$\bar{\gamma}_h = \bar{\gamma}_{if} = \bar{\gamma}_{ef} \quad (11)$$

$$V_{or}' = V_{e.}' = V_e' \quad (12)$$

$$V_{or}'' = V_{e.}'' = V_e'' \quad (13)$$

$$P_i = P_h \quad (\text{set condition}). \quad (14)$$

Now

$$\Delta V_{e.} = \Delta V_{or} = \Delta V_{i.} + \Delta V_h \quad (15)$$

or

$$\Delta V_{i.} = \Delta V_{e.} - \Delta V_h = \Delta V_{or} - \Delta V_h. \quad (16)$$

Then

$$\Delta V_{i.} = (\bar{\gamma}_{or} V_{or}' - \bar{\gamma}_h V_h') \Delta x. \quad (17)$$

From (11)

$$\Delta V_{i.} = \bar{\gamma}_h (V_{or}' - V_h') \Delta x. \quad (18)$$

But

$$V_{i.}' = V_{e.}' - V_h' = V_{or}' - V_h'. \quad (19)$$

Therefore, from (18) and (19),

$$\Delta V_{i.} = \bar{\gamma}_h V_{i.}' \Delta x \quad (20)$$

or

$$\frac{\Delta V_{i.}}{\Delta x} \frac{1}{V_{i.}'} = \bar{\gamma}_h \text{ or } \frac{dV_{i.}}{dx} \frac{1}{V_{i.}'} = \gamma_h. \quad (21)$$

But

$$\bar{\gamma}_h = \frac{\Delta V_h}{\Delta x} \frac{1}{V_h'} \text{ or } \gamma_h = \frac{dV_h}{dx} \frac{1}{V_h}. \quad (22)$$

Combining (21) and (22)

$$\frac{\Delta V_{i.}}{\Delta V_h} = \frac{V_{i.}'}{V_h'} \text{ or } \frac{\Delta V_{i.}}{V_{i.}'} = \frac{\Delta V_h}{V_h'}. \quad (23)$$

In the limit as $\Delta V_h \rightarrow 0$,

$$\frac{dV_{i.}}{dV_h} = \frac{V_{i.}}{V_h} \text{ or } \frac{dV_{i.}}{V_{i.}} = \frac{dV_h}{V_h}. \quad (24)$$

The ratio between the variation of the volume of the interior of the container (i) and that of the container (h) is equal to the ratio between their respective volumes when the pressure in the interior equals that of the exterior. This relationship would hold equally well if the pressure medium inside the container (or host, h) is replaced by a solid isotropic inclusion (i) at the same pressure. Thus (24) becomes equivalent to (5).

A third way of arriving at the desired volume relationship applies to a particular geometric form, thereby losing some generality. This method has certain advantages, however, in maintaining a physical picture. In figure 1, (a) and (b) represent the cross-sections of the same container discussed under the second method for determining (5), (9), and (10) at two different states of expansion (with the exception of its particular geometric form). In figure 1 let both host (h) and cavity (i) be cubic in outline with cube edges perpendicular to and parallel to the plane of the page. The infinitesimally narrow orifice (0) maintains the set condition of pressure equality between h and i. Then in the first state (figure 1a),

$$V_h' = \phi^3 a^3 - a^3 = a^3 (\phi^3 - 1) \quad (25)$$

and

$$V_{i.}' = a^3. \quad (26)$$

ϕ equals the ratio of an outside cube edge to an inside cube edge. After expansion (homogeneous in both position and direction) by the linear factor, Θ (multiplication by Θ is equivalent to a change of scale)

$$V_h'' = a^3 \Theta^3 (\phi^3 - 1) \quad (27)$$

and

$$V_{i.}'' = a^3 \Theta^3. \quad (28)$$

Now

$$\Delta V_h = V_h'' - V_h' = a^3 (\phi^3 - 1) (\Theta^3 - 1) \quad (29)$$

and

$$\Delta V_{i.} = V_{i.}'' - V_{i.}' = a^3 (\Theta^3 - 1). \quad (30)$$

It follows that

$$\frac{\Delta V_h}{V_h'} = \Theta^3 - 1 \quad (31)$$

and

$$\frac{\Delta V_{i.}}{V_{i.}'} = \Theta^3 - 1. \quad (32)$$

Combining (31) and (32), (23) is obtained. The remaining reasoning is the same as before.

Effect of departures from (5) on pressure relationships.—It follows from the condition for maintenance of pressure equality that a higher fractional expansion for an inclusion relative to the host for a given positive change in some external variable (from condition of pressure equality)² will result in a higher pressure in the inclusion than the mean pressure in the host. This will result from the constraining effect of the host. A given negative change in the same external variable will result in a relative decrease of the pressure in the inclusion. If the inclusion has a *lower* fractional expansion for a given positive change in the external variable, the pressure relationships will be reversed for corresponding departures from the condition of pressure equality. In this paper contraction is considered as negative expansion.

Assuming that the inclusion, once included in the host, behaves as a closed compositional system, the only coefficients of expansion (phase transitions are not considered) that could affect the pressure relationships between the inclusion and the host with changing conditions of temperature and pressure are the coefficients of compressibility (β) and the coefficients of thermal expansion (α). Definitions of these coefficients are:

$$\beta \equiv - \left(\frac{\partial V}{\partial P} \right)_T \frac{1}{V} \quad (33)$$

and

$$\alpha \equiv \left(\frac{\partial V}{\partial T} \right)_P \frac{1}{V} . \quad (34)$$

It is appropriate to consider an example. Let an inclusion be at the same pressure (P') and temperature (T') as its host. Let $\alpha_i > \alpha_h$ and $\beta_i > \beta_h$. Then, in accord with the above discussion, at constant external pressure, a given increase in temperature will result in a relatively higher fractional expansion for the inclusion and hence relatively higher pressure for the inclusion. Likewise a given decrease in temperature causes a decrease in the pressure of the inclusion relative to that of the host. At constant temperature a given increase in external pressure will result in a relatively higher fractional *contraction* (i.e. lower fractional expansion), and hence lower relative pressure for the inclusion (β is taken as the *negative* of the fractional expansion with respect to pressure). A decrease in external pressure will result in higher relative pressure for the inclusion. Table 1 summarizes the dependence of the pressure relationships on the expansion coefficients and position of the assemblage in P-T space relative to a point where $P_i = P_h$.

Under certain circumstances where a solid inclusion withdraws from the host crystal, it is doubtful that the pressure difference for the simple combination in the laboratory could exceed one atmosphere (the difference between a vacuum and the pressure of the atmosphere). Observation of features in the host that are sensitive only to stress differences much greater than one atmosphere would, in the case of withdrawal, not be observable. If the inclusion clings to the host mineral, the minimum value for the radially directed least stress will be governed by the strength of bond of the inclusion to the host. In the case of expansion of the inclusion relative to the host the maximum value

² Other variables are held constant.

TABLE 1

Pressure relationships between inclusion and host relative to P-T point satisfying relationship, $P_i = P_h$, in different situations

Relations of pressures to P-T point			Constant
Low pressure side	High pressure side		
$P_i > P_h$	$P_i < P_h$	$(\beta_h - \beta_i) < 0$	T
$P_i = P_h$	$P_i = P_h$	$(\beta_h - \beta_i) = 0$	T
$P_i < P_h$	$P_i > P_h$	$(\beta_h - \beta_i) > 0$	T
Low temperature side	High temperature side		
$P_i < P_h$	$P_i > P_h$	$(\alpha_h - \alpha_i) < 0$	P
$P_i = P_h$	$P_i = P_h$	$(\alpha_h - \alpha_i) = 0$	P
$P_i > P_h$	$P_i < P_h$	$(\alpha_h - \alpha_i) > 0$	P

for the radially directed greatest stress will be governed by the resistance to fracturing of a host crystal. This resistance will in turn depend, in part, on the distance of the inclusion from the surface of the host crystal and the size of the inclusion, in addition to the unit strength of the host.

Extension of the relationship, $P_i = P_h$, in a P-T diagram.—It remains to deduce the extension in a pressure-temperature diagram of the condition of pressure equality between host and inclusion. Thus, if no material is added to or subtracted from the assemblage,^a

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP. \quad (35)$$

Then, from (33) and (34), (35) becomes

$$dV = V\alpha dT - V\beta dP = V(\alpha dT - \beta dP). \quad (36)$$

From (36)

$$\frac{dV_i}{V_i} = \alpha_i dT_i - \beta_i dP_i \quad (37)$$

and

$$\frac{dV_h}{V_h} = \alpha_h dT_h - \beta_h dP_h. \quad (38)$$

From (5), (37), and (38),

$$\alpha_i dT_i - \beta_i dP_i = \alpha_h dT_h - \beta_h dP_h. \quad (39)$$

Now $P_i = P_h = P$. Also, from the nature of the physical situation, $T_i = T_h = T$. Therefore

$$(\beta_h - \beta_i) dP = (\alpha_h - \alpha_i) dT. \quad (40)$$

^a Actually the "host" need not be the whole of the crystal surrounding an inclusion. It is necessary only that the host be that part of the surrounding crystal that developed at essentially the same P and T as that of inclusion. Growth of the surrounding crystal through an extended P-T range poses some interesting problems that are not considered in this paper.

Thus

$$\left. \frac{dT}{dP} \right|_{P_1=P_h; T_1=T_h} = \frac{\beta_h - \beta_1}{\alpha_h - \alpha_1}. \quad (41)$$

Equation (41) is the desired relationship. Although it applies to a different physical situation, it is identical in mathematical form to the equation deduced by Ehrenfest for the variation of the temperature of a transition of the second order with pressure (see Guggenheim, 1949, p. 285-287).⁴

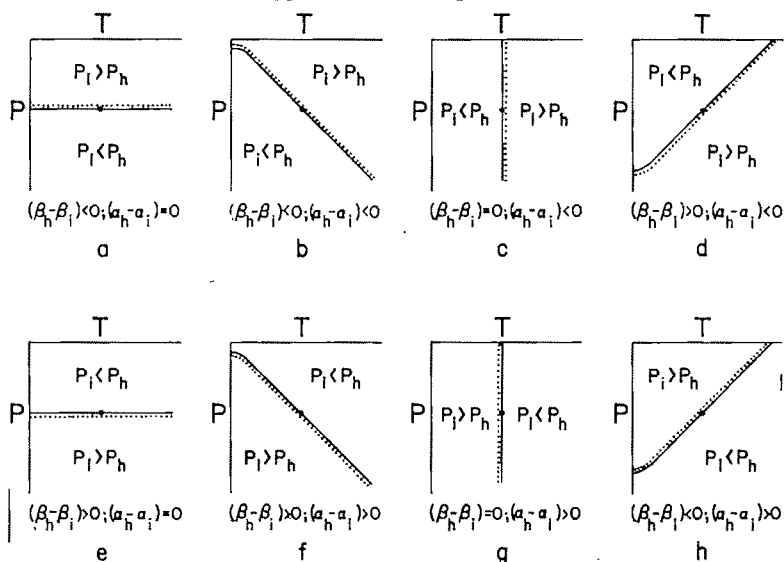


Fig. 2. Schematic diagrams illustrating dependence of pressure differences between host and inclusion on temperature, pressure, and the relationships between coefficients of thermal expansion and compressibility.

Relationship (41) is the differential equation of a line in a pressure-temperature diagram along which the pressure in an isotropic inclusion (the inclusion may be a fluid) is equal to that of an isotropic host. On one side of a line delineated by (41), $P_1 > P_h$; on the other side, $P_1 < P_h$. Determination of the pressure relationships of inclusion to host on either side of the line is identical to determination of these relationships to a point (cf. table 1). Consideration of one point on the line establishes the P-T areas in which $P_1 > P_h$ and $P_1 < P_h$. In figure 2 the solid lines indicate schematically lines along which $P_1 = P_h$ and the relationships of their slopes to $(\beta_h - \beta_1)$ and $(\alpha_h - \alpha_1)$. The dotted lines indicate the sides of the P-T lines on which $P_1 > P_h$. It is worth noting that a line of the type appearing in figure 2 could be used as an identifying criterion for either host or inclusion if one is a known mineral.

⁴ It is also the equation applicable to maintenance of the "straight" position for a bi-metallic strip formed by bonding straight strips of two metals with contrasting properties ($\Delta\beta$ and/or $\Delta\alpha$ large) to one another at a given pressure and temperature. Possibly the bimetallic strip has been overlooked as a useful thermometric-piezometric device in experimental work at high temperatures and pressures. Two such strips, with contrasting values for dT/dP in accord with equation (41) and appropriate electrical connections, conceivably could prove useful for thermometry and piezometry in high pressure bombs, especially where *path* in P and T is of concern (see also page 532).

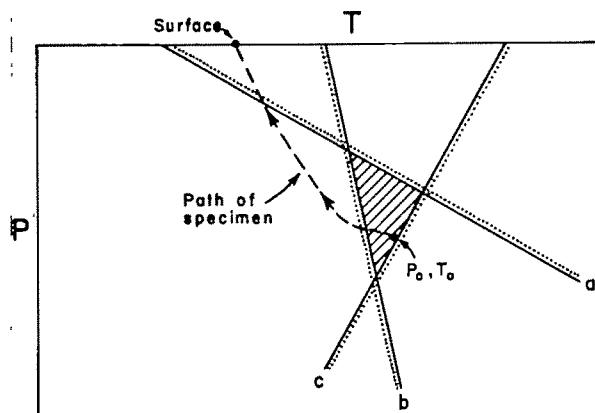


Fig. 3. Schematic diagram illustrating expected apparent pressure-temperature curves and their dependence on path if relaxation phenomena are important. See text for discussion.

Effect of creep or fracture on interpretation of P-T lines.—Before developing a possible method for utilizing knowledge of the existence of the above lines to determine P_0 and T_0 , it is proper to consider the possible effects of creep or fracture induced by expansion of the inclusion relative to the host crystal. In general, if the path in P-T shifts subsequently to inclusion at P_0 and T_0 (indicated by small open circles on P-T lines of figure 2) into the region where $P_1 > P_h$, any decay in the radially directed maximum stress due to creep or fracture will result in shift of the *apparent* position of the experimentally determined P-T curve into the area (relative to the original P-T curve) where $P_1 > P_h$ (area containing dotted line in figure 2). Under this circumstance the apparent curve would not pass through P_0 and T_0 . Location of such a curve by any experimental method will therefore indicate only that the *true* P-T curve lies at some unknown position on the opposite side of the apparent P-T curve (i.e. opposite to the side where $P_1 > P_h$). By using various combinations of host and inclusion it should, in principle, be possible to delimit an area within which P_0 and T_0 must lie. Such an area (shaded) is indicated schematically in figure 3, where the convention is the same as that of figure 2. Actually, in figure 3, curves a and b are most likely to be apparent P-T curves, as the path crosses them in the direction of the fields where P_1 is greater than P_h . Therefore, P_0 and T_0 are most likely to lie at some position on curve c between curves a and b. If curves a, b, and c were to meet at a point, that point would most certainly represent P_0 and T_0 . It would furthermore probably indicate the absence of creep. Any relaxation due to fracture could be accounted for by actual observation of such fractures.

Another possibility exists for demonstration of the absence of creep. Referring to illustrations b and f in figure 2, let two host-inclusion pairs crystallize simultaneously at P_0 and T_0 , one pair consisting of phase x as an inclusion in host y and the other pair consisting of phase y as an inclusion in host x. If the two curves are identical in position (except for "facing" as indicated by dotted line), it is presumptive that there has been no creep.

The above reasoning leads to a consistency test in cases where a number of apparent curves of the type discussed in figure 3 is known for a particular host containing a number of different kinds of inclusions. P_o and T_o may not lie within any closed area for which $P_i > P_h$ for one or more of the bounding curves. The absence of a closed area within which $P_i \leq P_h$ with respect to each of the bounding curves indicates data inconsistent with single values for P_o and T_o for all inclusions in the particular host.

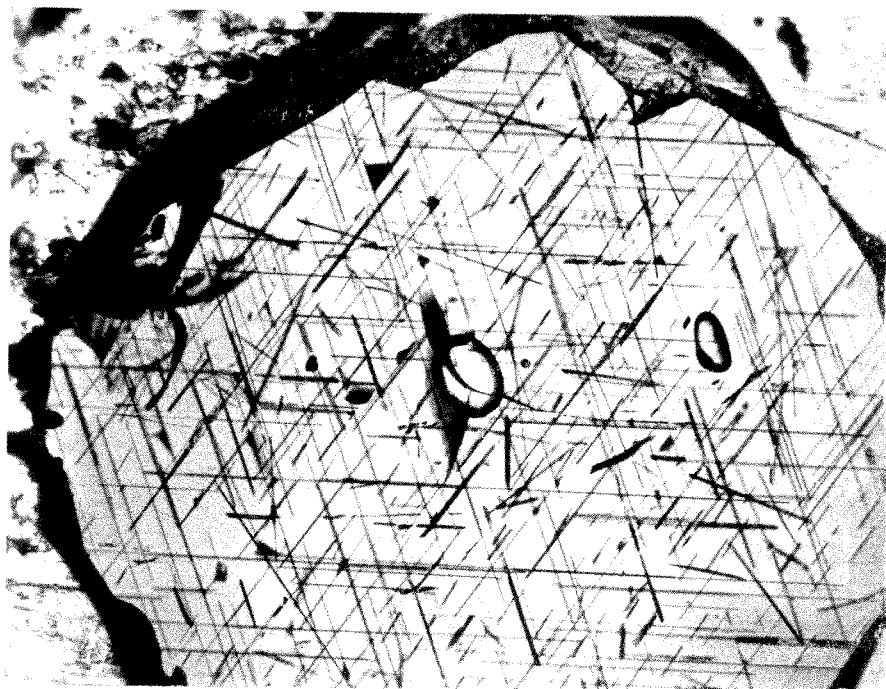
POSSIBLE EXPERIMENTAL METHODS FOR DETERMINING P-T CURVES⁵

Phenomena functionally related to pressure difference between host and inclusion.—A first requirement in the geological application of the above ideas to the practical problem of determination of pressures and temperatures of inclusion is the observation of physical phenomena in a host phase that are functionally related to the pressure difference between host and inclusion. This study had its origin in the examination of just such phenomena. In garnets from the Navajo Indian Reservation of northern Arizona (acquired from Burnham Mineral Company, Monrovia, California; kindly called to our attention by K. D. Watson), the writers have observed pronounced birefringent haloes around many different included minerals. The interpretation that the birefringent haloes are probably the result of stress is supported by the fact that, in one specimen, a birefringent halo disappeared when an inclusion was broken away from the host crystal. Many of the haloes are associated with radial fractures. In one case, radial fracturing occurred in garnet around an inclusion following grinding to a thickness of about 0.8 mm. The fractures, which were not seen when the garnet was first examined after polishing, appeared within a one-hour period. Photomicrographs of this specimen appear in figure 4. The radial fractures appear around the inclusion at the center of figure 4a. In figure 4b crossed polarizing filters permit observation of the birefringent halo around the same inclusion. The oriented inclusions in the garnet of figure 4 appear to be rutile.

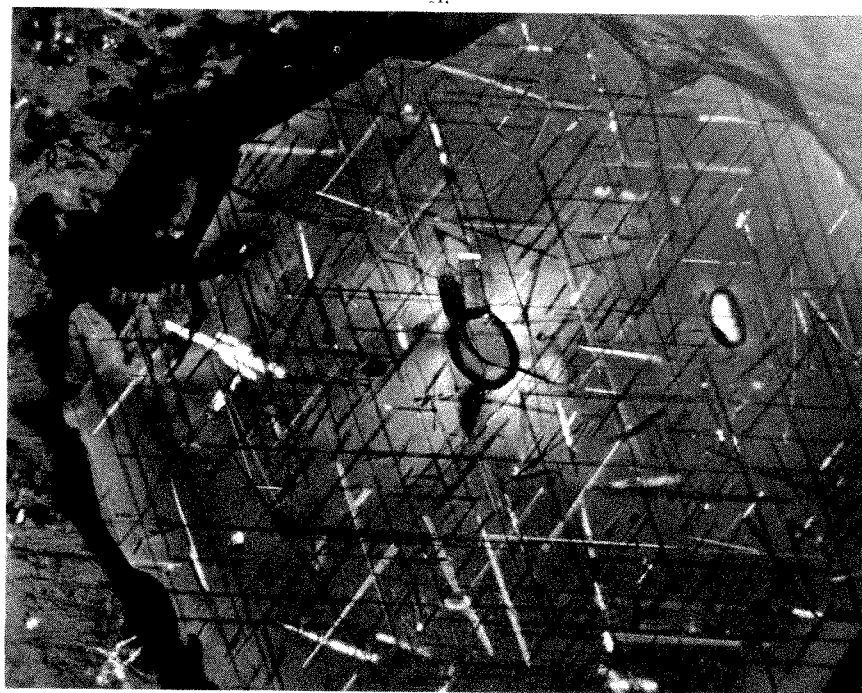
Check with compensator plate indicates that the low index is approximately radial to the inclusion in each of the observed birefringent haloes. In terms of piezobirefringence, this would indicate that the maximum principal stress is radial in all cases where such haloes have been observed by the writers (Poindexter, 1955, p. 1053). This confirms the conclusion deduced independently from the presence of radial fractures. In figure 5, a particularly intense birefringent halo appears around a small inclusion. Crude attempts with a hand-forced probe resulted in reproduction of birefringent haloes with low refractive index radial. Calculations based thereon (i.e. (stress difference) $\approx$ (force)/(area of probe point)) suggest that many haloes represent stress differences of the order of 10^4 to 10^5 bars (i.e. the breaking stress).

Optical null technique using window bomb.—The advantage of null measurements in observational procedures have long been recognized (Wilson, 1952, p. 882), particularly in the case of comparative measurements. The writers suggest the following as one possible procedure for mapping P-T curves (condition: $P_i = P_h$) for one transparent isometric mineral that includes an-

⁵ The writers intend to seek support for an experimental program to extend this study.



A.



B.

Fig. 4. Photomicrographs of garnet showing stress phenomena. (a) Garnet with radial fractures around crystalline inclusion (plane polarized light; magnification: 21.4X); (b) Same viewed between crossed polarizing filters showing piezobirefringent halo.

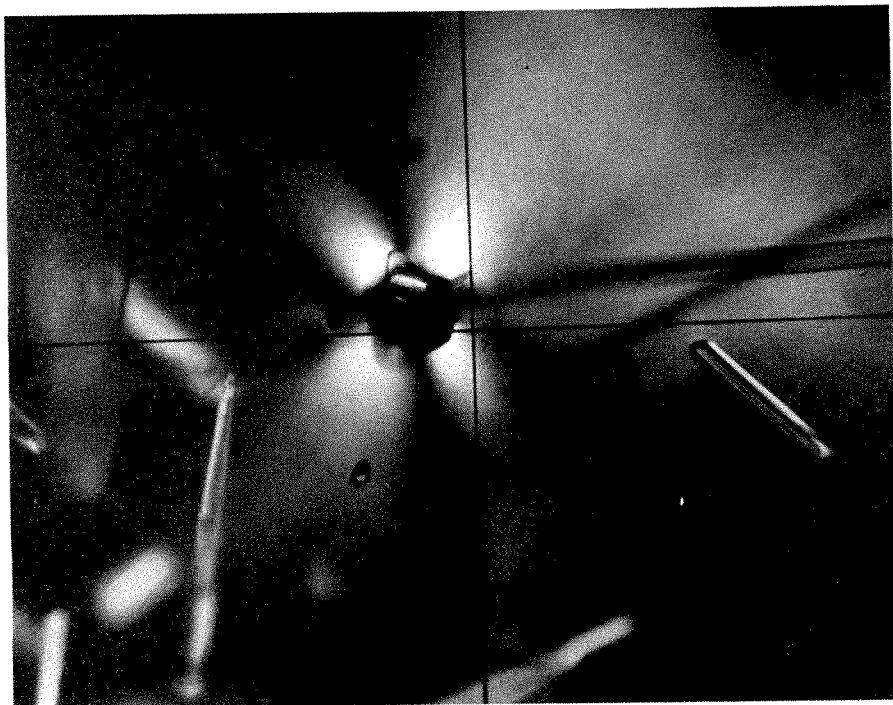


Fig. 5. Photomicrograph showing intense piezobirefringent halo around inclusion in garnet (crossed polarizing filters; magnification: 112X).

other isometric mineral. Let the assemblage be placed in a window bomb⁶ in such a manner that it can be observed between crossed polarizing filters by means of transmitted light. Let the pressure and temperature be simultaneously adjusted until a point on the boundary of the P-T field where $P_1 > P_h$ is determined by nulling the birefringent halo. By successive repetitions of this procedure at different pressures and temperatures it should be possible to locate a sufficient number of points to define the P-T curve. By carrying out similar operations for different combinations of host and inclusion in a rock, it should be possible to delineate more than one such curve and find an intersection. In the absence of creep or fracture the intersection would represent P_0 and T_0 . These relationships are indicated schematically in figure 6. Validity of extrapolation of the curves outside the experimental range of the bomb would be governed by the straightness of the lines and the precision with which they are located. Some measure of the validity of any extrapolation might be provided by the proximity of a number of such curves to a particular point in a P-T diagram.

It might be objected that isometric minerals are not elastically isotropic and that therefore the above procedure would not be valid. It is true that isometric minerals are not isotropic in regard to all their elastic properties, but it

⁶ Dr. Leason H. Adams informs the writers that window bombs of sufficient capacity and capability for moderately extended pressure-temperature ranges have been available for some time.

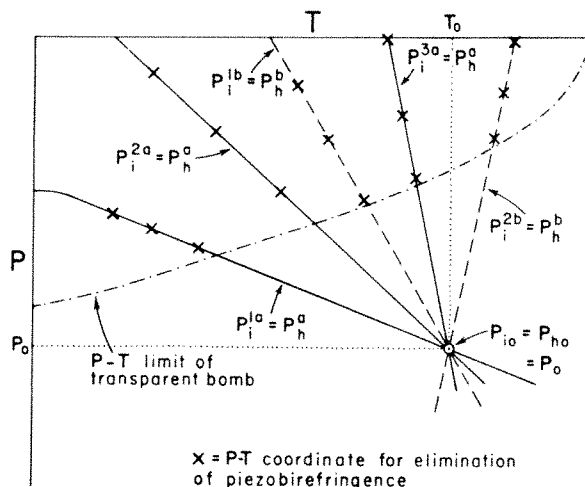


Fig. 6. Schematic diagram to illustrate determination of P_0 and T_0 . Subscripts: numbers identify inclusions; letters identify hosts.

is also true that they can be treated as isotropic solids under the restriction that they are subjected only to temperature changes and variations in hydrostatic stress (i.e. pressure). Nye (1957, p. 147) says that "in the cubic system the linear compressibility is isotropic: a sphere of a cubic crystal under hydrostatic pressure remains a sphere." Also (Nye, p. 103, 23) a sphere of a cubic crystal remains a sphere when its temperature is altered. Both of these facts are most fortunate, for it is the case of hydrostatic pressure variation and temperature variation that is considered in using the null method, thereby avoiding thorny theoretical problems.

It should be noted that null piezobirefringence should occur at all points around a nonisometric mineral included in an isometric host (assuming no creep) only at P_0 and T_0 . Disallowing withdrawal, at all other values for P and T piezobirefringence should appear at some points adjacent to the inclusion. Although the writers have considered the situation only superficially, it is possible that the null methods discussed here might be applied to study of tetragonal, hexagonal, and trigonal inclusions in isometric hosts or reciprocal combinations. The combinations would presumably be viewed in the directions of principal symmetry axes of the nonisometric crystals. In this paper emphasis on isometric combinations results from the considerably greater ease with which they can be analyzed theoretically.

Optical null technique using heating or cooling microscope stage.—A second experimental method would make use of a heating or cooling microscope stage and values of α and β for both host and inclusion determined over an extensive range of temperatures. Assumption of constancy for the ratio, $(\beta_h - \beta_i) / (\alpha_h - \alpha_i)$, allows calculation of P-T straight lines from equation (41). With this method an attempt would be made to locate a temperature of null piezobirefringence by observing the assemblage between crossed polarizers as the temperature is varied. Linear extrapolation of the P-T curves from any

null temperature would then be based on use of equation (41). Although the transparent bomb procedure is to be preferred, much useful information with little investment could result from this latter approach. Combination of the two procedures would, of course, provide an experimental check on the utility of extrapolations based on equation (41). The technique using the simple heating stage would work only if the P-T curve for the assemblage intersects the available temperature range at atmospheric pressure.

Auxiliary electrical null techniques.—A supplementary approach to determination of the P-T curves for a particular host-inclusion combination could be carried out by using one of the above methods in combination with more readily available pressure-temperature bombs. This approach would make use of the fact that two columns of equal length of materials A and B, regardless of their shapes in a lateral direction (A might be the material of an inclusion and B the material of the host; each could consist of a stack of slices if necessary), will satisfy a desired volume relationship, equation (23) (from which (5) follows), if equality of lengths is maintained as P and T are varied. Fitted to the context of the present problem,

$$\frac{V_{A1}-V_{A0}}{V_{A0}} = \frac{V_{B1}-V_{B0}}{V_{B0}} \text{ OR } \frac{\Delta V_A}{V_{A0}} = \frac{\Delta V_B}{V_{B0}}, \quad (42)$$

where the subscripts, 0 and 1, indicate two different states. It is necessary to prove that (42) is a direct consequence of the relation:

$$S_A = S_B \quad (43)$$

where S is the length of the indicated rod. Then

$$S_{A0} = S_{B0} \quad (44)$$

and

$$S_{A1} = S_{B1}, \quad (45)$$

from which it follows that

$$\frac{\Delta S_A}{S_{A0}} = \frac{\Delta S_B}{S_{B0}}. \quad (46)$$

Consider rods A and B to be composed of close-packed small unit cubes of edge, r , with one of the principal cube edges in each rod parallel to the long direction (S).

Then

$$S_A = m_A r_A \quad (47)$$

and

$$S_B = m_B r_B, \quad (48)$$

where m indicates the number of unit lengths determining the length of the indicated rod. From (47) and (48) it follows that

$$\frac{\Delta S_A}{S_{A0}} = \frac{m_A \Delta r_A}{m_A r_{A0}} = \frac{\Delta r_A}{r_{A0}} \quad (49)$$

and that

$$\frac{\Delta S_B}{S_{B0}} = \frac{m_B \Delta r_B}{m_B r_{B0}} = \frac{\Delta r_B}{r_{B0}}. \quad (50)$$

From (45), (49), and (50)

$$\frac{\Delta r_A}{r_{A0}} = \frac{\Delta r_B}{r_{B0}}. \quad (51)$$

Let

$$V_A = n_A r_A^3 \quad (52)$$

and

$$V_B = n_B r_B^3, \quad (53)$$

where n indicates the number of unit cubes in the indicated rod. Then

$$V_{A0} = n_A [r_{A0}^3] \quad (54)$$

and

$$V_{A1} = n_A [r_{A0}^3 + 3(\Delta r_A) r_{A0}^2 + 3(\Delta r_A)^2 r_{A0} + (\Delta r_A)^3]. \quad (55)$$

Thus

$$\frac{\Delta V_A}{V_{A0}} = \frac{3(\Delta r_A) r_{A0}^2 + 3(\Delta r_A)^2 r_{A0} + (\Delta r_A)^3}{r_{A0}^3} \quad (56)$$

or, simplifying,

$$\frac{\Delta V_A}{V_{A0}} = 3 \left(\frac{\Delta r_A}{r_{A0}} \right) + 3 \left(\frac{\Delta r_A}{r_{A0}} \right)^2 + \left(\frac{\Delta r_A}{r_{A0}} \right)^3. \quad (57)$$

Similarly

$$\frac{\Delta V_B}{V_{B0}} = 3 \left(\frac{\Delta r_B}{r_{B0}} \right) + 3 \left(\frac{\Delta r_B}{r_{B0}} \right)^2 + \left(\frac{\Delta r_B}{r_{B0}} \right)^3. \quad (58)$$

Substitution from (51) and combination of (57) and (58) leads to equation (42), the desired relationship.

The electrical circuitries of the devices illustrated in figures 7 and 8 represent Wheatstone bridges designed to indicate the equality of lengths of A and B inside a P-T bomb. In the Wheatstone bridge of figure 7 there are two equal resistors (R) outside the bomb and two resistors (the "slide-wires", R_A and R_B) that are attached to the ends of A and B. The equality of resistances between D_A and E_A on the one hand and D_B and E_B on the other (the arrows D_A and D_B represent electrical contacts attached to the walls of the device) will indicate equality of lengths for A and B as these lengths vary with changing P and T. The equality of the resistances will, in turn, manifest itself externally in a null reading on the galvanometer (G). Thus all values of P and T that result in a null reading of G lie on a desired P-T curve. In both figures 7 and 8 insulators are indicated by the letter I. The device of figure 7 consists essentially of two slide-wire piezometers, hooked "in parallel", of the type with which Bridgman (1952, p. 156-157) made his very accurate measurements of the linear compressibilities of a number of crystalline solids. The device in figure 8 differs from that of figure 7 with respect to the manner in which the Wheatstone Bridge is unbalanced when $S_A \neq S_B$. Any inequality results in the severance of one arm of the bridge and a *discontinuous* shift in the galvanometer reading from the null reading. Two lights (or galvanometers?) (L) of equal resistance are substituted for the two resistors (R) of figure 7. It is clear from the circuitry of figure 8a that the light on the left side will be brighter than that on the right side when $S_A > S_B$ and dimmer when $S_A < S_B$. In figure 8, D is a swinging plate hinged on the knife bearing, F. The screws (E) are electrical contacts that maintain contact with the conducting caps (H) when $S_A = S_B$. It is assumed that A and B are insulators. A weak spring (S) maintains bearing contact when $S_A \neq S_B$ and serves as an electrical conductor.

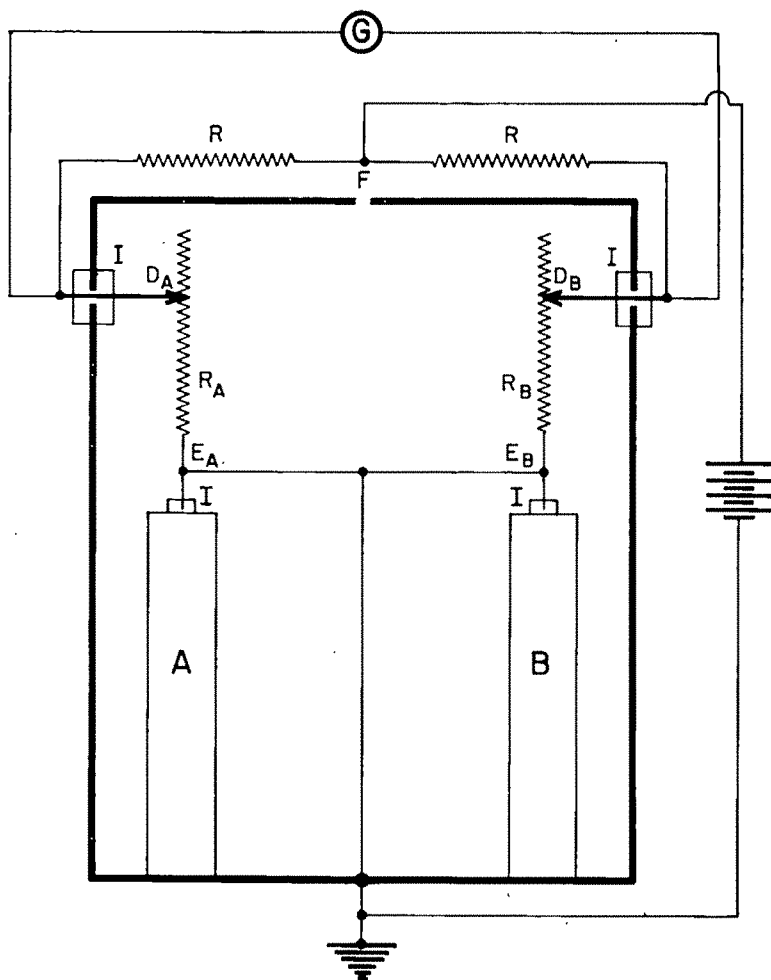


Fig. 7. Schematic diagram of device for determining P-T curves. See text for discussion.

Both C and D (diagonal patterns) should be conductors and should be of the same composition as the contacts, E. Bridgman's "levering" arrangement could be adapted to either of the devices figured.

Using either the device in figure 7 or that in figure 8, a family of desired P-T curves and an extensive coverage of a range of P-T conditions could be obtained by making successive null runs in P and T (in an inert gas medium) as the lengths of A and B at room temperature are made slightly different. Recovery of the equal length situation (and null position) would be by simultaneous adjustment of P and T. Normally a first run would be made from room temperature and atmospheric pressure. Then the rod with the larger coefficient of thermal expansion would be slightly shortened and the temperature at atmospheric pressure elevated until the rods had the same length as deter-

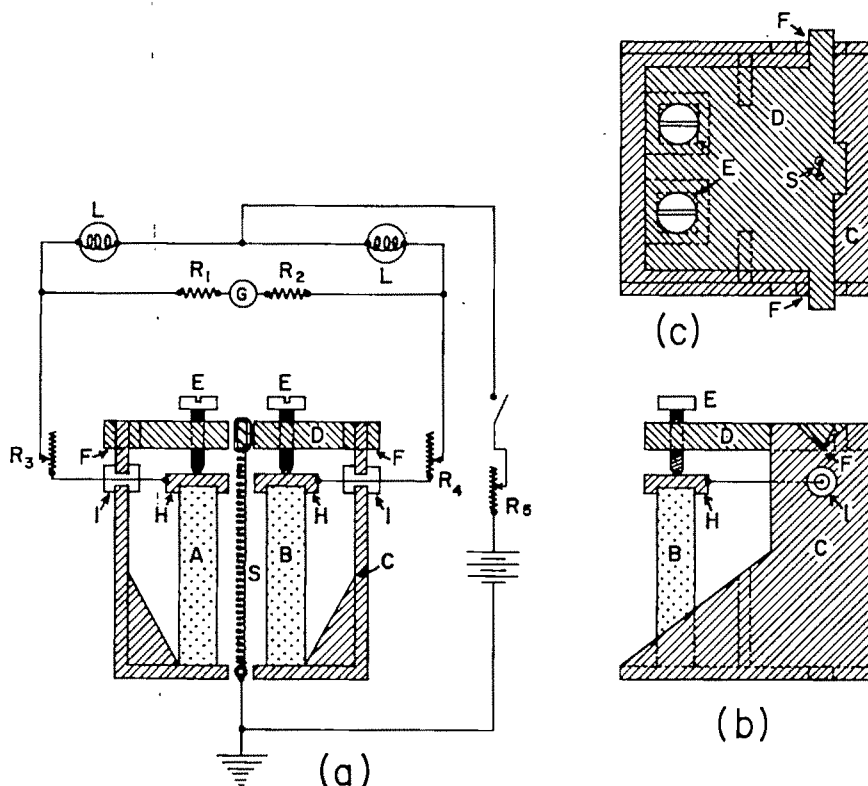


Fig. 8. Schematic diagram of device for determining P-T curves. See text for discussion.

mined by the null test. A second P-T curve would be obtained from this higher temperature in the same manner as the first. Other curves could be obtained in the same manner.

Application of this third approach to natural host-inclusion pairs would be by combination with the techniques using a window bomb or heating stage to locate a point on a P-T curve. Extension in P and T from this P-T point would be based on one of a family of curves determined by means of one of the electrical devices. The most suitable method or combination of methods for attainment of the greatest P-T range will have to be based on experience.

NATURAL COMBINATIONS AND INTERPRETATION

Previous descriptions.—The writers have done no experimental work as yet to facilitate the application to geology of the methods described above. In attempts to find geological counter-examples in order to test for applicability of the theory developed herein, it became apparent that numerous examples of stress phenomena around crystalline inclusions have been described. Sorby and Butler (1869, p. 295-297) appear to be the first to have observed and interpreted piezobirefringent haloes and radial fractures around crystalline inclusions as the result of pressure exerted on the surrounding host crystal

(i.e. $P_1 > P_b$). Some of the descriptions by them and others relate to rocks of great petrological and geophysical interest. Radial fractures around inclusions and birefringent haloes have been repeatedly observed in the diamond-bearing rocks of South Africa. Citations and descriptions are amply recorded in the classic studies of Sutton (1908, 1921, 1928) and Williams (1932, p. 420-429).

Advantages of study of diamondiferous rocks.—From the standpoint of the ideas developed in the previous sections of this paper, the associations from the well-described African kimberlites and eclogites seem best for initial study for the following reasons:

(1) The presence of diamond indicates that the pressure-temperature conditions of most recent crystallization or recrystallization are far removed from those of the near-surface environment in which they are observed. The thermochemical computations of Berman and Simon (1955), coupled with estimates of the Earth's thermal gradient, indicate pressures for diamond crystallization of over 50 kilobars (fig. 9). This would correspond to a probable depth in excess of 100 miles. Any inferred value for P_0 and T_0 for an inclusion in diamond would have to be located within the stability field of that mineral.

(2) Isometric minerals (besides diamond) are present, and there are numerous examples of host-inclusion relationships among these minerals. Thus Williams (1932) mentions the following isometric host-inclusion pairs:

<i>Host</i>	<i>Inclusion</i>
Diamond	Pyrope
Pyrope	Diamond
Diamond	Pyrite
Diamond	Magnetite
Diamond (one color)	Diamond (another color)

In addition, other minerals of the spinel group besides magnetite are associated with the diamondiferous rocks and have been found in diamond (Futergendler, 1958; Orlov, 1959) and pyrope (Smirnov, 1959, p. 26). It is possible that these spinels may also be found in host-inclusion relationship to the remaining minerals above. In addition, the following nonisometric minerals are listed as inclusions in diamond: ilmenite, olivine, biotite, graphite, chromian diopside, zircon, chlorite[?]. Bauer and Spencer (cited by Williams, 1932, p. 422) list as inclusions in diamond, in addition to the above: quartz [!?] (see also Orlov, 1959), topaz, and rutile. It is possible that those of the nonisometric minerals that deform readily under relatively small stress differences may be almost as useful for determination of P-T lines as isometric inclusions within an isometric host crystal. Creep might preserve the "hydrostatic" stress within the inclusion. Thus graphite, biotite, and possibly kyanite could prove useful.

(3) The mineral, diamond, has certain peculiar properties besides its isometric character that make it eminently suitable. These include:

- (a) its hardness, strength, and chemical inertness.
- (b) its transparency both to light and X-rays.

(c) the fact that its low values for α and β contrast so greatly with α and β for all minerals with which it is likely to be associated. This assures distinct stress effects in the vicinity of inclusions under most P-T conditions. These effects will be governed in part by any such contrast. This contrast, by the nature of (41), might also favor relative constancy of dT/dP for the P-T line satisfying the condition, $P_i = P_h$, and the experimental determination of its location.

(d) relative constancy of chemical composition (constant properties favored).

(e) its low scattering power for X-rays and small number of X-ray diffraction lines. This permits nondestructive identification of inclusions (and their orientation; cf. Mitchell and Giardini, 1953; Futergendler, 1958; Orlov, 1959). It may permit stress determination within the inclusions by allowing accurate determination of lattice spacings (Barrett, 1952, p. 316-335).

Making the crude assumption that the ratio, $(\beta_h - \beta_i)/(\alpha_h - \alpha_i)$, of equation (41) does not show major variations with P and T in the region of petrologic interest (relative to values calculated from data appropriate to the near-surface environment), it is possible to construct appropriate P-T lines emanating from hypothesized values for P_0 and T_0 . In figure 9 the straight lines represent lines of inclusion equilibrium ($P_i = P_h$) so determined from equation (41) for various combinations of host and inclusion found in the diamondiferous rocks of South Africa. The barbs on the small arrows indicate the sides on which $P_i > P_h$. In addition to isometric combinations, some com-

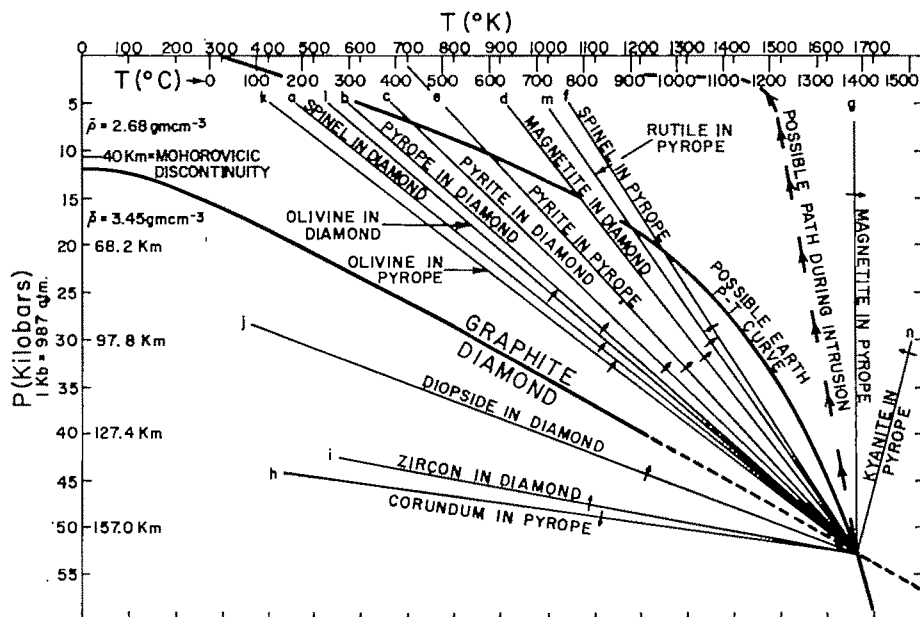


Fig. 9. Pressure-temperature diagram illustrating utilization of equation (41) to explain stress phenomena around inclusions. Diamond-graphite equilibrium from Berman and Simon (1955). See text for discussion.

binations, represented by crystals of lower symmetry in isometric hosts, are included. Coefficients of compressibility and thermal expansion used in determining the curves are taken largely from the compilations by Birch and Dane (in Birch, Schairer, and Spicer, 1942) and Verma (1960). P_0 and T_0 were selected to lie on a possible earth pressure-temperature curve at the graphite-diamond boundary (Berman and Simon, 1955). Selection of a point near the boundary is based on the presence of graphite inclusions in diamond (Williams, 1932). In view of the crudity of the assumptions on which figure 9 is based, it is almost surprising to find evidence of effects around inclusions that are consistent with some of the curves. Thus Sutton (1918; cited in Williams, 1932, p. 429-430) says: "A very fine diamond, weighing 42 carats . . . contains the most lovely inclusions one can imagine—one apparently a small garnet, another a honey-coloured zircon . . . of fair size. Through, and surrounding the position of, the supposed garnet is an extensive crack, while both above and below the zircon, and tangential to it, are similar cracks. These cracks are parallel to contiguous faces of the diamond, and neither reaches the surface of the latter [a picture of the zircon appears in: Williams (1932, v. 2, opp. p. 420)] . . . Under the polariscope a state of great internal strain is manifest over a large area in the region of the zircon by a most magnificent coloration, while the zircon itself is equally splendid. Words, indeed, are insufficient to describe the chromatic beauty of the polariscopic view. Curiously, there appears to be no strain to speak of in the vicinity of the crack through the garnet, as though the strain which once must have existed there and caused the crack had been relieved." In the context of figure 9 it is easy to explain the phenomena described above by Sutton, even allowing for considerable latitude in the location of P_0 and T_0 and the slopes of the relevant curves of inclusion equilibrium. Thus curve i indicates that a zircon inclusion should stress the surrounding diamond at surface pressure and temperature.⁷ Curve b indicates that pyrope garnet should not stress surrounding diamond under normal surface conditions. The cracks around the garnet are easily explained by the P-T path that the diamond must have followed during its eruption in the kimberlite. Kimberlites form breccia pipes that are believed to result from rapid eruption. Thus their eruption was probably an almost isothermal process (actually almost adiabatic with temperature decrease dependent on amount of expansion) followed by cooling in an almost isopiestic near-surface environment, as indicated in figure 9. The "dog's leg" path in P and T would carry the diamond-garnet host-inclusion pair into a P-T environment where the garnet could stress and fracture the surrounding diamond, following which there would be relaxation of the stress due to cooling.

Other examples of stress phenomena have been described from the diamondiferous rocks. Williams (1932, pls. 87, 110) shows photomicrographs of eclogite containing garnet with kyanite inclusions. The inclusions are clearly surrounded by radial fractures, indicating radial compressive stress in agreement with curve n of figure 9 (the properties of kyanite are not available, and those used for this curve are inferred from structurally similar topaz). Since

⁷ Subsequent to the writing of this statement, L. Silver suggested to the writers that this interpretation might be complicated by radiation damage related to the zircon (for example, see Ramdohr, 1960).

curves a, b, c, k, and l⁸ of figure 9 intersect the temperature axis at atmospheric pressure nearest to normal surface temperature, it will be most interesting to determine the piezobirefringent phenomena for these cases.

One important advantage of the inclusion method of P-T determination over present methods using P-T curves for phase transitions of the first order results from the fact that the P-T curves determined by the inclusion method are "tuned in" on P_0 and T_0 at some position in the Earth. This results from the very nature of the physical process of incorporation in a host. Pressure-temperature curves (ignoring activities of perfectly mobile components for the purposes of the present treatment) for first order phase transitions, on the other hand, are not determined by any situation in the Earth but only by the properties of the phases themselves. Thus, using the solid inclusion method, it should be possible in principle to pinpoint a large number of temperatures of crystallization at various depths in the Earth (assuming knowledge of a pressure-depth relationship) by examination of metamorphic rocks and inclusions imported to the surface by igneous eruptions. Since diamondiferous rocks have been transported to the surface the method offers some hope for determination of temperatures at specific depths within the Earth's mantle (fig. 9).

An advantage to be expected in metamorphic rocks.—The writers hope to explore the applicability of the methods described here to garnet in regionally metamorphosed rocks. In principle these rocks should present advantages for this type of study relative to study of rapidly erupted igneous rocks because of a straighter P-T path after recrystallization. The metamorphic rocks would probably follow a less complicated path more nearly coincident with the Earth's P-T curve in the area. Such a path might avoid the type of fracturing indicated for diamond around pyrope (see above), by showing lower penetration into the P-T area where $P_1 > P_h$.

Application of principles to other geologic phenomena.—The principles discussed in this paper are not limited in their application to inclusions of mineral grains in other mineral grains. They apply equally to large masses of rock included in other large masses of rock. Thus, for example, the unroofing of a granitic stock, recrystallized under metamorphic conditions, might be accompanied by stress phenomena around its walls and in its interior that are different from those around a granitic stock crystallized directly from a magma at shallow depths. The difference would probably be amplified by the quartz $\beta \rightarrow \alpha$ transition after solidification in the latter case. One would expect the paths in P and T after the last crystallization in the two cases to be far apart except at the surface, where the paths meet. Herein may lie one possible clue to the fact that certain granitic masses are characterized by well-developed sheet jointing more or less parallel to the Earth's surface, whereas others do not show this phenomenon. Contrasting properties of rock masses might allow

⁸ Orlov (1959, p. 104) presents pictures of piezobirefringent haloes around olivine crystals included in diamond and (p. 107) mentions observation of similar phenomena around garnet crystals in diamond. It should be noted that, in figure 9, curves representing garnet-diamond combinations should bracket surface temperatures. Under the assumptions implied in figure 9, the curve representing almandine in diamond would intersect the zero isobar at approximately 100° K. Because of considerable variations in the compositions of garnets coexisting with diamond, it is not surprising to find that some garnet inclusions exert radial compressive stress on surrounding diamond and some do not.

large stresses to develop during unroofing under conditions far removed from those under which plastic flow would relax such stresses.

The principles might also shed light on the origins of joints perpendicular to directions of elongation in areas of heterogeneous layered metamorphic rocks. The differential expansion or contraction subsequent to metamorphism might result in such joints and also account for the fact that these features, though later than the metamorphism, are commonly related in orientation to the structures associated with the metamorphism.

One of the most interesting facts emerging from this study is the evidence that certain minerals are able, without major relaxation, to sustain directed stresses approximating fracturing stresses over geologic time intervals. The writers are familiar with no other phenomena that so vividly illustrate this persisting strength of certain materials under the near-surface conditions in which they are found.

ACKNOWLEDGMENTS

Had it not been for the generous cooperation of K. D. Watson, who is currently engaged in a very interesting petrologic investigation of certain features of the "Four Corners" region (northeastern Arizona), the writers probably would not have become mindful of the phenomena upon which this paper is based at a time when they were prepared to utilize the information. He stimulated this study by providing garnet crystals for the "thick-section" study through which the writers first became aware of the possible petrologic utility of the piezobirefringent effect around crystalline inclusions in minerals. B. Weissberg suggested a way to reduce the number of steps between (36) and (41), and his help is gratefully acknowledged. These steps had previously been carried out in a more cumbersome fashion, using equation (9). The writers have further benefited extensively from discussions with G. P. Eaton, R. L. Shreve, and J. B. Thompson, Jr. Part of the work leading to the ideas developed here was supported by a grant from the Research Committee of the University of California (L.A.). Drafting was done by Opal Kurtz. Excellent "thick sections" were prepared by J. DeGrossé. Photomicrographs were made by J. Groom. The writers are particularly indebted to R. O. Castle and L. H. Adams for discussions during the preparation of this paper and critical reading of the manuscript. The writers also wish to thank H. Winchell for several suggestions he made for improvement of the manuscript.

Note added in proof:

After this paper had been submitted, the writers became aware of a very valuable compilation by Smith (1953), and it is desirable to acknowledge some of his prior thoughts with regard to the subject of this paper (p. 100, 110-111). The following prophetic quote is from the last page of his text (p. 111), and it might well have served as a takeoff point for the present paper:

"The temperature of fit of crystal inclusions in minerals could be determined by optical methods such as measuring the degree of distortion of the crystal structure of the host, say by strain birefringence or interferometry. . . . If the effect of pressure on the fit is large, then the temperature of fit of dif-

ferent orientations of anisotropic inclusions, and of different species of inclusions, will be different. In this case the temperature of fit could be determined at different pressures, until a unique temperature and pressure are found at which there is fit of all types of crystal inclusions. These values would be the temperature and pressure of crystallization of the host."

From the operations envisaged it is clear that his conditions of "fit" would satisfy the writers' relationships (5) or (23).

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THE PSEUDOTACHYLITE OF THE GAIRLOCH DISTRICT, ROSS-SHIRE, SCOTLAND

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ABSTRACT. During the closing stages of the Laxfordian orogeny the Lewisian basement complex of Gairloch suffered widespread crushing and shearing, which affected each of four different rock groups in a distinctive manner. A variety of crush veins were produced which vary in habit according to the environment of formation.

Many of the veins intrude the wall rock and bear convincing evidence of the movement of the vein material from its source in a crush plane to the relatively undisturbed host rock. Some of the veins carry structures, such as relic glass and spherulites, which indicate that part of the vein material was melted at the time of intrusion.

It is concluded that, although recrystallization and devitrification have largely obscured the evidence, true pseudotachylite exists together with ultramylonite in the Gairloch crush rocks.

INTRODUCTION

Recent mapping of the Lewisian basement complex in the Gairloch district of the Scottish North-West Highlands has revealed a widespread occurrence of crush veins (fig. 1) whose characteristics differ according to the nature of the host rock.

Clough (1907) noted at many localities in the North-West Highlands, including Gairloch, the presence of "flinty crush-rock" which he described as having a dull, aphanitic, and structureless appearance, as being typically black or brown in color, and as occurring within zones or areas of shearing within the Lewisian. In the Gairloch district (lying within the prominent crush-belt "A" in fig. 1), he noticed that the crush veins sometimes bulge into rounded projections or end bluntly, having the appearance of intrusive felsites, and he speculated on their possible origin by frictional fusing.

Jehu and Craig (1924) described extensive pseudotachylite development along the great thrust zone in the Lewisian Gneiss of the Outer Hebrides. This is the only other occurrence described from the British Precambrian rocks, but the thrusting movements causing the pseudotachylite formation are considered to be associated with the Moine Thrust (of Caledonian age) on the mainland (Kuresten, 1957) and are therefore much later than the crush belts in the mainland Lewisian, which have long been established as Precambrian in age.

The name *pseudotachylite*¹ was first applied to the intrusive crush veins of Parijs, South Africa (Shand, 1916), where the country rock (Precambrian granite-gneiss) is cut by numerous irregular black aphanitic veins, up to three feet in width, which exhibit intrusive relations and show spherulites, microlites, and "partly-melted felspars". These phenomena were taken by Shand to indicate local frictional melting of the host rock and subsequent intrusion of the resulting liquid.

Later work has cast some doubt on whether the Parijs crush rocks were actually intruded as a liquid. Willemse (1937) found that the rock still appeared granular under very high magnification and failed to establish the

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¹ A comprehensive review of the terminology of fine-grained crush rocks appears in an account of the mylonites of the San Andreas Fault Zone (Waters and Campbell, 1935).

presence of glass. X-ray diffraction analyses gave a pattern characteristic of a crystalline powder of ultra-fine grain. Waters and Campbell (1935) had earlier shown that much of the evidence cited by Shand and others in favor of the melt hypothesis could be explained in other ways.

Obviously, where a glassy crush rock of great age is concerned, devitrification is to be expected and the resulting rock will be difficult to distinguish from a crush rock which has never been anything more than a powder. Under these conditions, and in view of the extremely close packing of the tiny inclusions, conventional chemical, optical, or spectrographic methods give ambiguous results.

That melted crush rock does, however, occur has been convincingly shown by Scott and Drever (1953), who described completely undeformed vesicular glass from a Himalayan thrust zone. The relatively recent (probably Tertiary) date of this occurrence is the likely explanation for its survival in this form.

GEOLOGICAL SETTING

The Lewisian basement complex of Gairloch comprises many different rock types, all highly deformed, in varying stages of metamorphism. For the purpose of this paper, it is convenient to distinguish (without stratigraphical implication) four broad groups of rocks (fig. 1): (A) semipelitic schists, (B) acid gneiss with parallel foliation, (C) acid gneiss with irregular foliation, and (D) hornblende schist, each of which responds in its own manner to deformation.

The deformation which produced the crush rock phase occurred after the latest period of metamorphism and constituted the closing stages of the Laxfordian orogeny (see below). The schistosity is broken and folded by the crushing movements, and the crush veins themselves are broken by a further series of fractures which also formed under the Laxfordian stress system.

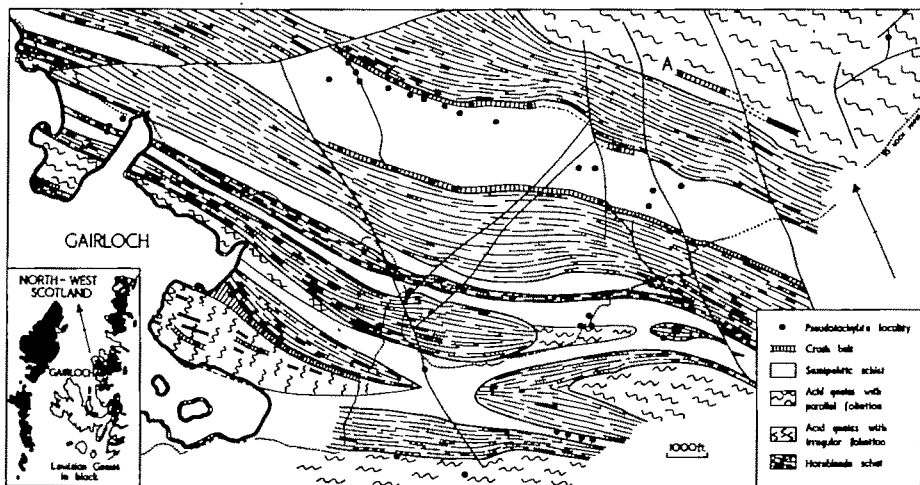


Fig. 1. Map showing the distribution of crush belts and pseudotachylite localities in relation to the approximate outcrop of the four main rock groups.

The crush movements affected the four rock groups as follows (fig. 1):

(A) *Semipelitic schist*.—Belts of strong shearing and crushing with extensive pseudotachylite formation are developed along the boundary planes of the main schist belt and to a lesser extent on other lithological boundaries. In addition, there are many crush vein localities sited within belts of shattered schist or as isolated patches throughout the area.

(B) *Acid gneiss with parallel foliation*.—The prominent belt of crushing in the NE quadrant of the map contains abundant crush veins. Otherwise, crushing is confined to scattered short bands or isolated patches, a few of which exhibit pseudotachylite and most of which lie near a lithological boundary.

(C) *Acid gneiss with irregular foliation*.—A relatively small wedge-shaped area in the west has yielded to the deformation in a distinctive manner because of the lack of vertical planes of potential shearing. Subparallel vertical crush belts have been formed at frequent and almost regular intervals and often contain crush veins and pseudotachylite.

(D) *Hornblende schist*.—No crush belts appear in any of the numerous bodies of hornblende schist, the deformation of which is taken up by shearing along the closely spaced schistosity planes or by movement along the boundaries.

Crush veins also occur in the fracture zones of some of the large trans-current faults, the earlier movements of which are penecontemporaneous with the concordant shear or crush belts.

THE CRUSH VEINS

Habit

All stages can be traced between crush veins that lie within, and are obviously genetically related to the mylonized crush belts (fig. 2a), and those that show wholly discordant and indeed intrusive relations with their wall rocks, which are mineralogically and structurally unaffected by the crushing movements (fig. 2d.). Intermediate stages (illustrated in figs. 2b, c) show crush veins lying only in part concordant with the schistosity and in places sending out discordant branches.

Crush veins exhibit a marked range of habit according to the type of host rock in which they are found. Two prominent types can be conveniently distinguished although transitional types exist:—

Branching veins (fig. 2d).—These are characteristic of rock group (A) and typically show marked intrusive relations. The individual veins tend to be thicker and to have a relatively small proportion of inclusions (especially large ones) in the matrix. Iron ore is abundant. Clear isotropic patches are not readily apparent and devitrification is strongly expressed.

Net veins (fig. 2f).—These are characteristic of rock groups (B) and (C) and show a network habit of thin intersecting veins which for the most part follow a pre-existing set of cracks and show little evidence of intrusion. The ratio of inclusions to matrix is very much higher than in the branching veins and iron ore is much less evident. Small clear isotropic areas occur and devitrification is uncommon. Transitional types of net veins (fig. 2e) show some of the features of the branching veins and in particular have a relatively high proportion of dark, fine-grained matrix.

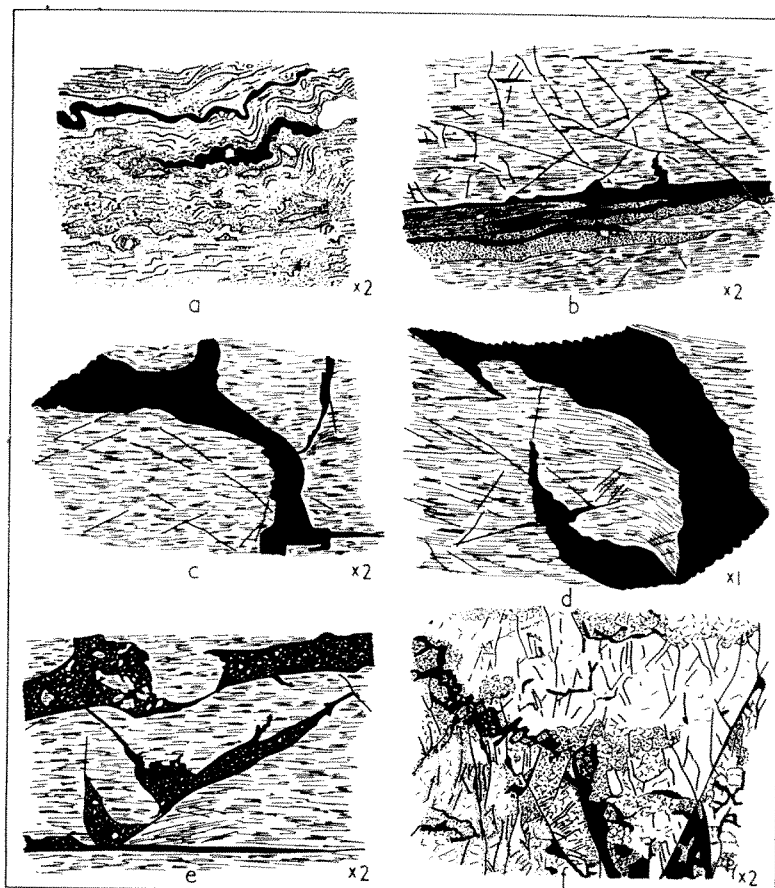


Fig. 2. Types of crush vein, (a) Mylonite with concordant crush vein approximately in site of formation, (b) Concordant crush vein showing flow structure developed in iron-rich and iron-poor bands. Small apophyses intrude uncrushed host rock, (c) Concordant passing into discordant crush vein, (d) Completely discordant intrusive crush vein with branching veinlets, (e) Crush vein network in biotite-rich gneiss, (f) Crush vein network in fractured quartzo-felspathic gneiss.

These differences are related to the relative abundance of biotite in the schists compared to the gneisses; and to the tendency of the quartzo-felspathic gneisses to fracture along discordant cracks and of the schists to split more readily along the schistosity planes.

Whether the biotite was fused or merely powdered, it may be inferred that conditions normally existed for the relief of the stressed rock mass before the disintegration or fusion of the quartz and felspar had proceeded very far, and the crushed mass was able to flow and intrude, carrying the bulk of the original quartz-felspar content with it. Thus the ability of the more biotite-rich crush rocks to flow was greater. On the other hand, the system of cracks in the quartzo-felspathic gneisses provided convenient existing channels for the vein material.

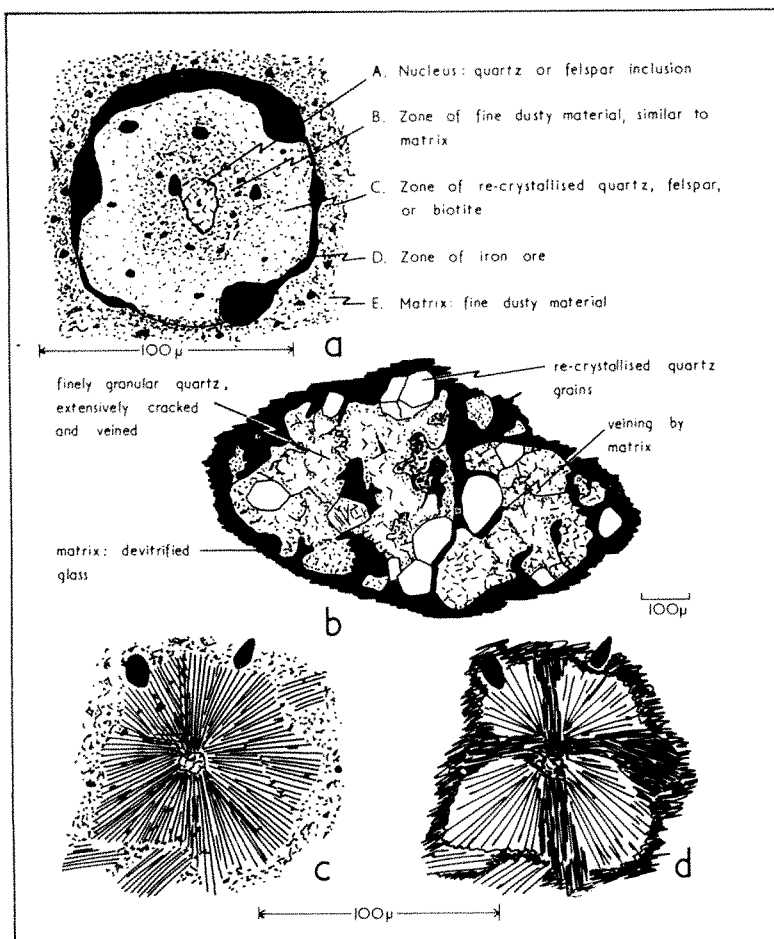


Fig. 3. Types of structures within pseudotachylite. (a) Diagram of typical spherulite showing zonation. (b) Partly recrystallized inclusion showing veining and corrosion by the matrix. (c) Radially arranged biotite microlites. (d) The same, under crossed nicols, showing typical black cross.

Some of the crush veins (mostly branching veins) studied in detail are concluded to be, in part at least, true pseudotachylite. It is likely that many of the examples seen only in the field are also pseudotachylite, and that both ultramylonite and pseudotachylite exist commonly and in association in the area.

Recrystallization of the Crush Vein Material

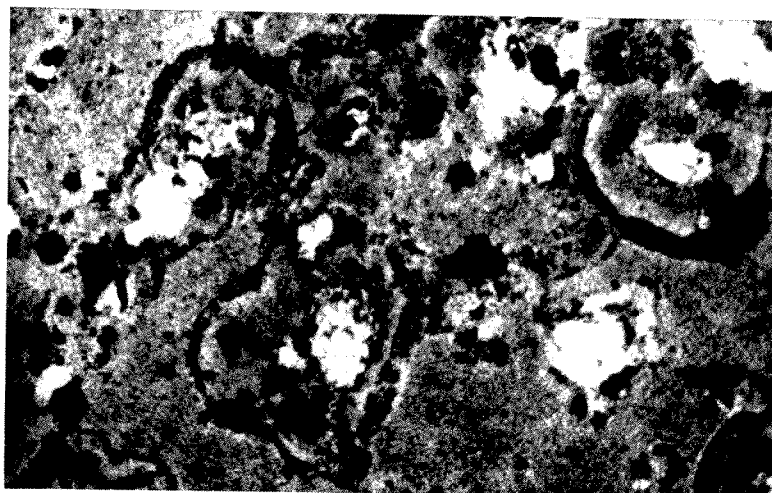
Extensive recrystallization can be observed in most of the veins. In some of the thicker veins the matrix consists in places of a felted mass of recrystallized biotite flakes. Usually the orientation of these crystals is random, but occasionally radially arranged microlites occur (fig. 3c, d). Magnetite, present as a fine dust, often shows good crystal outlines and may cause a zoned ap-



A. Mylonite with concordant crush vein approximately in site of formation (see fig. 2a) (X 8).



B. Completely discordant intrusive crush vein with intrusive veinlets (see fig. 2d) (X 5).



C. Spherulites (see fig. 3a) (X 250).

pearance of the veins due to its concentration in bands, especially at vein edges. This effect is caused by the selective recrystallization of biotite, which absorbs the iron ore during its growth. Recrystallization of quartz and feldspar is commonly shown where an inclusion is replaced partly or wholly by a mosaic of recrystallized grains. In the matrix also, similar replacement may be deduced from the existence of ill-defined patches with continuous extinction and low first-order interference colors.

Evidence of Flow in the Crush Veins

Many of the crush veins (pl. 1-B, fig. 2b, c, d) show indisputably, by their mode of branching with blind-ending veinlets, that the vein material has been intruded into its present position and has not been formed in situ. Supporting evidence comes from the coexistence of highly abraded, strained quartzes—products of extreme crushing—and wall rock comparatively free from shearing and crushing, implying transport of the vein material from its site of formation in a crush plane. Further, the alignment of inclusions and the redistribution of iron-ore-rich parts into parallel bands (fig. 2b) show that the vein material has flowed into place. The absence of mineralogical downgrading at the vein wall indicates that heat accompanied the intrusion.

Evidence of Melting in the Crush Veins

Evidence of melting is shown by a variety of structures: (a) Small patches or veinlets of clear, pale green or pale brown, isotropic material (glass) are occasionally present where the inclusions are not quite so dense and where recrystallization has not occurred. Such clear glass is found only in the thin net veins in the acid gneisses. (b) Spherulites (pl. 1-C, fig. 3a) and radially arranged microlites (fig. 3c, d) are found in a few of the thicker veins in schist and are thought to be products of initial crystallization from a melt. (c) Devitrification is common as is shown by the finely granular appearance of the matrix (not in itself proof of devitrification), the finely granular, dusty-looking, inner zones of spherulites (fig. 3a), and the mosaic effect of the groundmass where it has recrystallized (as in some devitrified igneous glasses). (d) Embayed and veined inclusions, common in the thicker veins (fig. 3b), seem to be the result of magmatic corrosion. (e) Occasionally the biotite in the vein material has crystallized out in a unit and completely fills the vein from wall to wall, enclosing the xenoblasts.

The spherulites (fig. 3a) vary considerably in appearance but in general consist of four concentric zones: the nucleus, which is usually present, consists of an inclusion of quartz (mostly), feldspar, or iron ore, often partly or wholly recrystallized; the fine granular zone, also usually present, consists of subisotropic material similar to that outside the spherulite and thought to be devitrified glass, or perhaps, in some cases, very small recrystallized grains replacing the radial microlitic growth of the original spherulite; the recrystallized zone, which is invariably present, its circular form defining the spherulite, consists of small crystals of quartz, feldspar, or biotite, sometimes radial in habit, and occasionally extending into the nucleus; and the opaque ore zone, which is

generally present except where biotite is the recrystallizing mineral, consists of densely packed iron-ore grains forming a narrow peripheral ring.

The zonation is most easily explained on the assumption that most of the spherulites formed around inclusions that already possessed a rim of glass deposited by the surrounding liquid and that then acted as a nucleus for the typical radial crystallization of the spherulite proper. In the case of quartz or felspar the process was accompanied by the expulsion of the unwanted iron-ore dust to the periphery of the growing structure. When the whole cooled, the surrounding matrix vitrified, becoming indistinguishable from the inner glassy zone. Later devitrification of the glass and recrystallization of the presumed radial fabric of the spherulite produced the present rather indeterminate structure which only fragmentarily, by the presence of the outer ring and by the occasionally preserved relics of an original radial pattern, discloses its mode of growth.

GENESIS AND AGE

Almost all the known occurrences of pseudotachylite occur either in Archaean basement rocks or in granites. The significant common factor is great depth at the time of formation. Thrusts which occur nearer the surface are without pseudotachylite even although the relative movement involved was enormous, as in the case of the Moine Thrust, where the total frictional heat was much greater than in many pseudotachylite-bearing crush zones.

The limitation of the pseudotachylite to the deeper parts of the crust may be explained by the relatively high temperatures accompanying the crushing. The great depth of cover may have caused a reduction in the rate of loss of the heat accumulated by the friction, and very sudden movements may have produced a rapid increase in temperature. The rocks were certainly cool enough to be rigidly deformed by fracturing both before and after the pseudotachylite formation, and so the necessary rise in temperature to produce local melting must have been due solely to the crushing movements.

The formation of the pseudotachylite can be envisaged as occurring as part of a sequence of events comprising the closing stages of the Laxfordian orogeny. As the complex became more rigid after the close of the metamorphism, continuing stress operating in a NE-SW direction caused the shearing movements on schistosity planes (which had previously been the dominant mode of deformation) to give place to fracturing, crushing, and brecciation along both concordant and transcurrent planes. The fragmentation culminated in some cases in the production of bands of varying length and thickness containing ultramylonite, which was locally melted and intruded into the surrounding rocks. Further fracturing followed this episode before the whole complex was covered unconformably by the Torridonian beds.

The age of the pseudotachylite may thus be determined accurately in relation to the other structural events in the area, the chronology being shown in table 1.

TABLE 1
Unconformable deposition of Torridonian (Late Precambrian)

Large time gap	
L	Transcurrent faults
A	
X	Discordant shearing and fracturing
F	Concordant " " " }
O	
R	Late pegmatites
D	Metamorphism and vertical NW-SE
I	schistosity
A	
N	Folding

The Laxfordian of Gairloch can be traced southwards into the Torridon area where it was equated with the type Laxfordian of Laxford Bridge in Sutherland (Sutton and Watson, 1951). Recent age determinations of Laxfordian rocks from Laxford Bridge (Giletti, 1959) give an average value of 1440 million years.

Because of the great age of the pseudotachylite, it is only to be expected that its glassy texture should have undergone extensive devitrification and that conclusive evidence of its former existence should be lacking.

ACKNOWLEDGMENTS

The writer's thanks are due to Dr. D. R. Bowes of the Department of Geology, University of Glasgow, for his encouragement and help, and to Professor T. Neville George for correction of the manuscript.

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ESSAY REVIEW

Recent Sediments, Northwest Gulf of Mexico. A symposium summarizing the results of work carried on in Project 51 of the American Petroleum Institute 1951-1958; F. P. SHEPARD, F. B. PHLEGER and T. J. H. VAN ANDEL, editors. P. 394 (14 papers), 205 figs., 12 pls. of marine invertebrates. Tulsa, 1960 (American Association of Petroleum Geologists, Box 979, Tulsa, Okla., \$6.00).—Prior to the arrival of the shock troops of API Project 51, three "cardinal principles" of Gulf Coast geology had been enunciated by students of the recent sediments of the area: (1) sealevel has not been much higher than it is at present during the last 5000 years (i.e., no evidence here of a Hypsithermal rise of sealevel), (2) weight of sediment causes subsidence of the crust under the Mississippi delta; and (3) the Mississippi delta is not a typical "textbook" or "Gilbert" delta consisting of topsets, foresets, and bottomsets, but is composed mostly of subaerial topset beds that are characterized by a pattern resembling superposed leaves formed by linear sand bodies (veins of the leaf, deposits of river channels), and intervening finer-grained sediments (of the interchannel areas).

The large task force of scientists of API Project 51 addressed themselves to collection of data on Recent sediments of the Gulf of Mexico during the seven years (1951-1958) of their study. In the process they added critical information on these and other questions. Many reports have been issued on different aspects of the work; the present volume is a final symposium report that contains both reviews of earlier work and new contributions. Gulf Coast geology and sedimentology in general will never be the same again as a result of this colossal undertaking.

One is easily overwhelmed by the sheer bulk of the data that they have assembled; digestion of it is difficult. Fortunately, the present book makes great strides toward assimilation and several papers in it are devoted solely to this aspect of the subject.

On first opening the volume this reader was struck by the fact that the title on the cover uses *Recent*, but all papers within employ the European term, *Holocene* (doubtless reflecting the influence of van Andel).

In this review I can only sketch out large areas of interest to me and possibly other sedimentologists and discuss briefly the contributions made to them by the Gulf of Mexico study group. As this project contains something in it for just about everybody, I cannot hope to cover its entire scope.

The subject of sealevel changes is discussed in separate papers by Shepard and by Curray and is also considered in the biologic papers by Parker and by Phleger; it also appears in the summaries by van Andel and by van Andel and Curray. Radiocarbon dates on littoral shell material provide the essential control for dating the events of the last 18,000 years. Prior to 18,000 B.P. the sea stood at about -65 fathoms; littoral drift patterns (judged by heavy minerals and distribution of faunas) were the same as those at present (essentially counterclockwise, with local clockwise drift north of the mouth of the Rio Grande river). This pattern results from the prevailing southeast winds. In the interval -18,000 to -16,000 years, the sea rose to about -45 fathoms with unchanged littoral drift pattern. From -16,000 to -12,000 years sealevel stood

still or possibly regressed slightly. Toward the end of this interval sealevel rose to about -25 to -22 fathoms without change in littoral drift direction.

The interval -12,000 to -11,000 years provides correlation with the Two Creeks and Allerød intervals of the glaciated regions. After the -25- to -22-fathom stand, the sea regressed to about -35 fathoms as the Mankato glacial advance occurred. Littoral drift patterns were reversed, indicating that the prevailing winds in the Gulf must have shifted from southeast to southwest. Between -11,000 and -10,000 years, the climate changed, the Mankato glaciers retreated, and sealevel began to rise again. The interval -10,000 to -7000 years marks a time of rapid sealevel rise and a return of the counterclockwise littoral drift patterns in the Gulf. After reaching a position of -10 fathoms, sealevel regressed once more to about -21 fathoms and the littoral drift pattern returned to clockwise. A new transgression followed to a stillstand at about -9 fathoms and littoral drift resumed its counterclockwise habit.

At approximately -7000 years, sealevel began a rapid rise and reached its present level about 3000 years ago (a recent revision from the previous figure of 5000 years).

Evidence from the Texas bay sediments and littoral features supports the contention that sealevel has not been much higher recently along the Gulf Coast, hence reaffirming the first "cardinal principle" of the Gulf Coast geologists. The record of sealevel changes also strongly supports the interpretation of sealevel behavior proposed by Fairbridge and is opposed to the school of continuous gradual rise without stillstands or regressions. The effects of these changes of level on continental shelf sediments are discussed in a paper by Curray.

The two other "cardinal principles" of Gulf Coast geology have not fared so well in the hands of API Project 51. Scruton first challenged the older Russell & Russell and Fisk school of interpretation of the Mississippi delta by his analysis of the delta sediments in terms of the classical concept of topsets, foresets, and bottomsets. Shepard has extended Scruton's analysis in more detail, particularly by his subdivision of the topset sediments. The delta has been shown to consist largely of fine-grained marine shallow-water foreset beds, which advance forward over the thinner bottomsets (which in turn overlies relict sands of the open Gulf, at least east of the delta). The topsets become important after forward delta growth has built up the pile to sealevel. Because southward advance of the delta has carried it to the very edge of the continental slope, further foresets and bottomsets here will be deposited in very deep water and rapid forward growth will effectively stop. Further subsidence without change in position of the distributary system, therefore, could cause the topsets to become thick as inferred by the superposed leaf concept, if sedimentation kept pace with subsidence. But, the general principle that even a marine delta built into shallow water must clearly emphasize the importance of foresets and bottomsets, which was previously denied, has been definitely established by API Project 51.

Other penetrating insights into delta behavior are also provided by Scruton and the others in their analysis of the effects of delta destruction by marine agencies as well as by their results on forward delta growth. Sheet sand

bodies are produced by residual concentration effects of the waves operating on the sand that is present in minor amounts within in the complex of generally finer-grained delta sediments.

A much clearer picture is now available as to what the sediments of a large marine delta are like. Doubtless more such complexes will shortly be identified in the stratigraphic record as a consequence of API Project 51. In the opinion of the reviewer, the "Catskill delta," long the alleged classic example of an ancient marine delta, will be the first to suffer from these results, for it simply does not fit into the pattern of a modern marine delta that has emerged from this study of the Gulf of Mexico.

Binocular microscope examination of the coarse fractions of entire sediment samples has been particularly valuable in delineating sediments from the different environments near the delta and elsewhere. Earlier papers by Scruton and by Shepard contain the details; they are also summarized in Shepard's delta paper in the present volume. The value of coarse-fraction examination is a new contribution of API Project 51; formerly size analysis began by dissolving away the shell materials (which have proved so diagnostic) in order to sieve uncontaminated quartzose residues.

The question of subsidence *versus* sedimentation has become a *cause célèbre* in the Gulf Coast. The Gulf school insists that sedimentary loading causes subsidence of the Earth's crust. Shepard, however, reports shallow-water shells in water deeper than their usual depth range on the shelf 60 miles east of the Mississippi delta in an area of negligible sedimentation. The most likely explanation of this observation is subsidence, for slopes here are not steep enough for gravity displacement downward and waves would tend to throw the shells landward. Radiocarbon dates from these shells permit the calculation of an average rate of subsidence of 1.2 foot/century, about the same figure computed for the thickest part of the delta where supposed early Nebraskan shallow marine sediment was reported by others at -4200 feet in a boring located at the end of South Pass. The subsidence rate here was calculated by Shepard to be a little less than 1 foot/century based on an assumed length of the Pleistocene of 500,000 years. In both localities the rate of subsidence is essentially equal; off the distributary mouths, however, rate of sedimentation has kept pace with subsidence.

A few more general sedimentologic "sacred cows" have also been slain by API Project 51; most of these concern the supposedly unique relationship between tectonism and sedimentation and the widespread denial and ridicule of the so-called "physiographic and oceanographic" approach to sediments.

The papers by van Andel, by Curray, and by van Andel and Curray emphasize that mineralogic composition of sand grains is primarily a function of their source, and that texture is a function of the environment in which they are deposited. These results support Folk's insistence on separation of grain mineralogy from texture in sandstone classification. A further item is the demonstration that in the Gulf of Mexico the distribution patterns of sand and clay fractions are different and completely independent of each other. In fact, the sand at one locality may be derived from one source, whereas the clay may come from a different source. Various mixtures of types of sediment that have

been held by some to indicate unique tectonic settings (such as graywacke and orthoquartzite) have been found alongside each other in various parts of the continental shelf.

The API study has emphasized that sediments consist of minerals whose composition is chiefly dependent on source lithology, which are deposited in particular geographic localities called environments of deposition. These environments are characterized by different water motion, salinity, organic content, etc., but are physiographic entities that impress their peculiar textural and other features on sediment grains that may be delivered to them. Tectonism enters the depositional picture only in the question of preserving the complex of products that have been built in a series of different geographic environments.

This volume contains three valuable papers on organic aspects of marine sediments: a new contribution on phytoplankton production in the Mississippi Delta area by Thomas and Simmons and reviews and summaries of earlier work on macroinvertebrates by R. H. Parker and foraminifera by Phleger. Bays and lagoons and their sediments are also discussed in papers by Shepard and Moore and by Rusnak. A further contribution to formation of barrier islands is contained in a paper by Shepard. The volume is rounded out with an introduction by Shepard, a general discussion of the geologic setting of the Gulf of Mexico by G. E. Murray (not a member of Project 51), and a retrospect by Phleger.

This book is an absolute classic that should be on the desk of every sedimentologist, stratigrapher, and paleontologist. It is a valuable reference that will require long, serious, and repeated reading. Its general impact on geologists might have been improved had still more consolidation and elimination of repetition been exercised and if the presentation had been formulated around specific problems of sedimentology rather than by the regional and special topical approach that has been used. The book is profusely and beautifully illustrated and well written; careful editing has eliminated typographical and other errors.

JOHN E. SANDERS

REVIEWS

My Life and Times as a Physicist; by I. I. RABI. P. vi, 55. Claremont, California, 1960 (The Associated Colleges, \$2.75).—This book publishes two lectures given by Professor Rabi in October 1959. The first, delivered before an audience of college trustees and business leaders in Los Angeles, is about "The Scientist and the Statesman". The second, given in Claremont, deals with "Science and the Humanities at Mid-Century". Both essays contain important points that merit publication to a larger audience, but it must be a matter for infinite regret that Rabi has not yet written the book that should properly have the title that is here wasted. The life and times of physicist Rabi cover many aspects of the growth of twentieth-century science, and unless Rabi and Oppenheimer and several others write with their first-hand knowledge of what actually happened, the story will become overlaid with a mass of paper and anecdote that conceals all modern history.

The first essay tells of Rabi's struggle with the politicians and military leaders over their maxim, "The scientist should be on tap, but never on top", and shows how this led to absurd situations in the development of radar. Proceeding from this to the general issue he makes most clearly the point that it is now, in many ways, the scientist who is holding the purse strings of civilization and it is he who must play a direct role in the executive and administrative branches of government. A powerful Department of Science, with a cabinet post, seems both wise and necessary, and there is a growing feeling that the traditional reluctance of scientists to enter the political arena must belong to a previous, more luxurious age. My only quarrel with Rabi would be over his unspoken assumption that it is the qualified scientist or ex-scientist that must mesh with the world of politics. A Minister of Agriculture need not be a successful farmer, nor one of Education a fine teacher. Is it not possible that out of our present urgency there might arise a sufficiency of men for whom science was no closed book but who were professionals in its administration rather than in its execution? Scientists seem to have a morbid horror of being administrated by non-scientists, but perhaps it is hopeful that in another field the business men are being directed by their economists.

In the second essay, Rabi's theme is one already made familiar in C. P. Snow's "The Two Cultures and the Scientific Revolution". Similar points are made in exhibiting the tendency to warfare between the Sciences and the Humanities. The author's solution seems touchingly simple and naive—a suggestion that scholars should take a Sabbatical in the opposite area, for example, that the Professor of Physics should relieve himself in Greek Drama, and the medievalist in quantum mechanics. One cannot altogether dismiss the suggestion; many are the physicists who, acting on this principle, are surprisingly well up in Sanskrit literature or in Chinese Art, fewer (but noticeable) are the historians and philosophers who read *Scientific American*. Others play chess or build boats. It seems a little hard to squeeze this proper and intelligent leisure into some formal Sabbatical scheme. Since the author has shown from the first essay that we shall need a whole governmental scientific machinery, could he not allow that we bridge our gap between the sciences and humanities by training such people? A college subject, turning all the tools of the humanist upon the sciences, would unite fields, without wild artifice. Subjects such as the history of science, its sociology, psychology, economics and philosophy, are the very educational tools we need for training a scientific ambassador or administrator. It is strange that those of us working in these fields need more than all else the sort of information that might be in a book, properly entitled "My Life and Times as a Scientist", by I. I. Rabi.

DEREK J. DE Solla PRICE

Minerals of New Mexico; revised ed.; by STUART A. NORTHROP. P. xvi, 665, 1 folded map. Albuquerque, 1959 (University of New Mexico Press, \$10.00).—The book is an extensive discussion of the mineralogical, historical, and economic aspects of the minerals of the State. It is divided into three main parts: an Introduction, Descriptions and Records of Occurrence, and a List of Districts, Subdistricts, Camps, etc. Bibliography of 1302 titles, and a map of the mining districts of the State are also supplied.

The introduction is further subdivided into sections on Previous Work, Highlights in the History of New Mexico Mineralogy and Mining, and Economic aspects of New Mexico's Mineral Industry. The note on previous work is brief. Forty-three pages are given to the historical highlights; they are superb reference material and interesting reading. Mineralogical lists occupy about fifty-one pages in all, and Economic Aspects of New Mexico's Mineral Industry (thirteen): general; comparisons; trend of exploitation; all-time production; production in 1956; employment; citations of New Mexico mineral deposits.

Descriptions and records of occurrence take about 464 pages. Each species is introduced by a description in small type, including comments on abundance or rarity of some of the species. The listed localities are given by counties, then by district or township. In many cases, especially in the discussion of new finds, the locality is given in detail.

The comments on each occurrence include analyses and quotations from the literature or from relevant newspaper reports. Seventeen pages are given to quartz, and fifteen to a fascinating discussion of the history and occurrence of turquoise.

The separate list of districts is accompanied by a map showing their approximate locations. A good list of other maps is given in the text. The arrangement of species is alphabetical rather than chemical; this permits quick reference and complete cross-indexing within the text but separates the mineral groups. A list or index of minerals in crystal-chemical order would be a welcome improvement. Most of the information in the volume is well arranged and annotated, but more frequent references from the descriptions to the rest of the book would be helpful.

This fascinating and useful book, with its extensive bibliography, is surely the authoritative work on the subject. The historical section is not only valuable but interesting, and the descriptions contain an abundance of information.

PETER LEAVENS

Minerals of Arizona, 3rd ed.; by FREDERIC W. GALBRAITH and DANIEL J. BRENNAN. The University of Arizona Bulletin, vol. 30, no. 2. P. 116. Tucson, 1959 (University of Arizona Press, \$1.00).—The book is a list of the minerals of the State and their localities of occurrence. Some 374 species are arranged according to the Dana system; each species is introduced with a note in small type, giving chemical and physical properties. The mode of occurrence and names of varieties are given in regular type. In a few species special data or references are cited, where they relate specifically to the Arizona specimens. The localities are given by county, and by region or district. Sometimes mine, prospect, or formation are included.

The book is brief, and there is considerable range in the treatment of various species. For beryl, the localities are very closely given, with the mineral associations at each; three pages are devoted to the varieties of quartz, but the albite-anorthite series has no localities mentioned; it is merely "Abundant and widespread in the rocks of state." A reference to available maps would be helpful, for some districts and regions are difficult to find on

most maps. More cross-indexing, with common names and mining terms, would be appreciated by many.

The book is carefully written and represents much study. The notes on the occurrence of each species are especially helpful.

PETER LEAVENS

Lehrbuch der Tektonischen Geologie; by KARL METZ. P. viii, 294; 188 figs. Stuttgart, 1957 (Ferdinand Enke, 46 D.M.).—Professor Metz of the University of Graz in Austria appears to be the first in recent decades to publish in the German language a textbook of structural geology intended for beginning students. Many are the books on tectonic theory written by German, Austrian, and Swiss geologists since the pioneer synthesis of Suess, and Prof. Bruno Sander of the University of Innsbruck has published major works on tectonic methods that are widely known (if not too widely read) in America. But more elementary textbooks, like those we are accustomed to, have been lacking.

The book is divided into two main parts. In the first, Study of Rock Deformation, are discussed the elements of structural geology—folds, faults, joints, cleavage, etc. Geology in Austria is impregnated with Prof. Sander's geometric and kinematic concepts of rock fabric, and Prof. Metz has consciously built his description of the structural elements—and indeed the entire book—around these concepts, showing again and again how they illuminate structural relations. Many an American reader may thus find in the book (which is written in reasonably straightforward German) a simplified entryway into petrofabric ideas, may come to appreciate better their importance and analytical power, and may finally be led into a thorough study of the special literature. For Prof. Metz carefully states in his Preface that his book "neither can be nor wishes to be a textbook of petrofabrica," and he repeatedly refers the reader to Prof. Sander's books and articles for authoritative discussions.

This part of the book will also be valuable as a thesaurus of German terminology in structural geology, especially as Prof. Metz has systematically tried to indicate the corresponding English and French terms and has provided an index of more than 800 entries.

In the second part of the book, Structural Evolution of the Earth's Crust, Prof. Metz has wished to show how the structural elements can be variously put together to form a "world picture". Thus this part is largely concerned with tectonic theories concerning types of tectonic development, sources of energy, and above all causal mechanisms for orogeny. Prof. Metz has tried to present fairly the major theories now contesting the field, though not refusing to express his own opinions, e.g. that the very multiplicity of theories suggests that we do not yet have enough data to solve the problem. If, however, Sander's ideas dominate the first part, Stille's dominate the second, reflecting in this regard the current state of thought in the Germanic countries. Moreover, to this reviewer the jump from the discussion of detailed structural elements to that of whole kratons and orogenic belts seems too abrupt, as if the student were already expected to know how the elements are commonly associated in the individual parts of a major tectonic province.

Examples and references are naturally chosen largely, though by no means entirely, from the German literature and especially concern the Austrian Alps. The bibliography is, however, not complete; a number of works cited in the text are not listed or appear under a different year. Furthermore many references are to publications of rather limited distribution, such as the *Radex Rundschau* or the *Berg- und Hüttenmännische Monatshefte*.

The value of the work for the American structural geologist lies, however, in the excellent introduction it provides to German structural terminology and current tectonic ideas.

JOHN RODGERS

Map of the Aletsch Glacier in 1957; Sheet 3, About 42 x 31 in. Scale 1:10,000; Contour interval 10 m. Published 1960 by the Topographical Survey of Switzerland, Seftigenstr. 264 Wabern-Bern. (10 Swiss francs).—This unusual map is the first of four sheets, which together will constitute the most detailed map ever made of a major glacier and its drainage basin. The Great Aletsch, perhaps the most studied of the 1200 glaciers in the Alps, is an excellent selection for detailed treatment. The preparation of the map, including new air photography and control, is the work not only of the Topographical Survey but also of at least seven other organizations and numerous individuals. Special techniques were used to maintain accurate vertical control on areas of snow and firn. The detail shown is quite remarkable.

A feature of the map is the inclusion of historical data to this extent: the positions of the glacier margin at its maximum advance during the 19th century, and again at the time the Daun end moraine was built, are shown by colored lines, which also reflect accuracy of knowledge of those positions from place to place.

The negative economy of the glacier during recent decades is reflected in the form of the terminal zone. The map should be extremely useful in current glaciologic study and as a basis for comparison with maps to be made several decades hence.

The map, either flat or in folded form, is obtainable from the publisher.

R. F. FLINT

Darwin's Biological Work: Some Aspects Reconsidered. Centenary Essays by P. R. BELL, J. CHALLINOR, J. B. S. HALDANE, P. MARLER, H. L. K. WHITEHOUSE, and J. S. WILKIE; P. R. BELL, editor. P. 343. Cambridge, 1960 (Cambridge University Press, \$7.50).—This is one of the best and most interesting works to appear in celebration of the centennial of the *Origin of Species*, though much of its virtue lies in the fact that it calls attention to the enormous importance of some of Darwin's other work, published in the *Expression of the Emotions in Man and Animals* (1872) and in his various late contributions to plant physiology and genetics.

Bell gives an admirable account of Darwin's work on phototropism, conducted with his son Francis in the 1870's. The most important result was the demonstration that whatever causes the curvature of a growing plant, whose upper part is illuminated from one side, "transmits its effect to the lower part".

Bell, placing this discovery in its historic setting, gives an admirable account of the subsequent history in its full elaboration of this part of plant physiology. It may come as a shock to some contemporary students to find that the theory of natural selection and the use of the oat coleoptile as an object of experiment were introduced into science by the same man.

Whitehouse deals in a similar way with Darwin's main contribution to genetics, namely his studies of floral polymorphism in *Primula*, *Lythrum*, and other genera. In this case, although at last we understand the genetic complexity of the questions which Darwin defined, there are still unsolved problems of a perplexing kind.

The third essay on this kind of theme is by Marler, following up Darwin's ideas about the expression or communication of emotional states, and giving an admirable account of modern work on the subject. Here again, Darwin's originality appears in his principle of antithesis by which a number of seemingly arbitrary gestures indicating pacific or antiaggressive states are explained as the opposite of the kinds of movements that occur in fighting. Marler gives a vast amount of information on animal signalling and language, including a number of original observations on insular birds that suggest a kind of behavioral character displacement.

Challinor's essay, though a salutary warning, largely deals with that gloomy subject, the imperfections of the geological record. It is an enlightening piece of work; but since it discusses almost exclusively British examples, it appears more insular than it need be. Moreover, the unexpected fact that evolution appears in several of the few reasonably complete lineages that we know to consist of a drift in the position of the mode in a highly polymorphic population is noted without genetic or any other comment.

The only essay to deal with what most of us regard as Darwin's main contribution is that of J. B. S. Haldane on Natural Selection. Here we see the old master at work; further comment would be invidious.

The book concludes with an historical study by Wilkie comparing the positions of Buffon and Lamarck with that of Darwin. This essay is a learned and illuminating discussion, but it suffers somewhat from the failure of the author to appreciate the actual experience with the organic world of the figures of whom he writes. It is, however, clear from Wilkie's essay that a divergent attitude towards taxonomy underlay the difference between Buffon's and Lamarck's theoretical views.

The book as a whole is most stimulating and as such an appropriate memorial to Darwin.

G. E. HUTCHINSON

Publications Recently Received

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- The Nature of Science; by David Greenwood. New York, 1960 (Philosophical Library, \$3.75).
- The Story of Chemistry; by Georg Lockemann. New York, 1960 (Philosophical Library, \$4.75).
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PERMO-TRIASSIC DIASTROPHISM IN THE WESTERN CORDILLERAN REGION*

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ABSTRACT. Essentially continuous orogeny and epeirogeny in portions of generally subsiding orthogeosynclinal belts is further confirmed by study of latest Permian and Triassic in the Cordilleran region. Apparent absence of Lower and Middle Triassic in most of British Columbia and Alaska was recognized early, but was not interpreted in terms of important tectonism. Evidence of orogeny has been known in Nevada and central British Columbia. In the latter area, Upper Triassic unconformably overlies late Permian that was intruded by ultrabasic rocks. The same relationships exist in central Oregon except that there important acidic and intermediate plutons also exist. Wide absence of *recognized* Lower and Middle Triassic, presence of pre-late Triassic intrusions, angular unconformities, and character of coarse clastic material suggest that the latest Permian-earlier Triassic interval was one of complex diastrophism, plutonism, volcanism, and elevation of lands in much of the western Cordilleran belt. Fossiliferous early and medial Triassic marine sediments are nearly confined to the miogeosyncline northward from California and Nevada, but during late Triassic there was widespread transgression in the eugeosyncline with deposition of much limestone, other sediments, and local volcanic rocks.

Relationships of acidic to ultrabasic plutons, deformation, and metamorphism during most orogenic episodes in the Cordilleran region were complex. Late Jurassic ("Nevadan") age was long assumed for all the ultrabasic bodies until pre-Jurassic ones were discovered in central Oregon. Most of these, along with many more acidic ones, are now known to be pre-late Triassic as are some of those in British Columbia, but others in British Columbia, southeast Alaska, and California are apparently Jurassic and Cretaceous. Most of the ultrabasic rocks in Washington are not adequately dated. Folding, batholithic emplacement and regional metamorphism are all quite variable in age along, as well as across, mobile belts. Ultrabasic bodies are equally variable and, therefore, do not necessarily mark any single or first stage of geosynclinal foundering. Mobile belt histories appear so complex when studied in detail that even famous named orogenies such as Nevadan and Laramian become somewhat indistinct one from another. Therefore, most attempts at naming and correlation of still smaller-scale orogenic pulses have questionable merit, and perpetuation of the oversimplified textbook dogma of a generalized "geosynclinal cycle" is unwarranted.

INTRODUCTION

Modern studies of mobile belt histories have underscored the fallacy of the outmoded classic concept of single, long-uninterrupted subsidence of geosynclines abruptly terminated by but one, short-lived orogeny that was synchronous over a whole belt. Evidence clearly indicates multiple orogenic and epeirogenic events *throughout* the complex histories of mobile belts. As employed here, these belts comprise all the great linear zones of long-continued weakness in the crust— island arcs as well as mountain systems. Portions of

* The writer gratefully acknowledges permission of Humble Oil and Refining Company to publish this paper. The stimulation of many former colleagues in that company has contributed materially to the ideas expressed here. T. P. Thayer, L. R. Laudon and Marshall Kay read and criticized the manuscript; J. G. Koch assisted with drafting and bibliographic checking. The manuscript was initially prepared while the writer held a post-doctoral research appointment from the Wisconsin Alumni Research Foundation.

these that have received great accumulations of sediments and volcanic rocks during long histories of subsidence and diastrophism, i.e. geosynclines, are of particular interest in this discussion.

During the past decade the conviction has grown that sedimentary and volcanic materials deposited within volcanic (eugeosynclinal) portions of the great orthogeosynclines have been derived considerably from lands or islands *within* eugeosynclines rather than from ancient, high borderlands lying outside these generally subsiding belts. Such internal lands have been elevated both by volcanism and by diastrophism (Kay, 1951), neither of which were, as a rule, precisely simultaneous nor of equal intensity throughout the length of a given belt. Occasionally, severe orogeny raised rather large lands which contributed great volumes of sediment to adjacent submerged areas for considerable lengths of time. Such lands may have approached the formerly postulated ancient borderlands in size but differed significantly in not having been composed of ancient Precambrian crystalline rocks and in their location within the mobile belt. Much sediment in eugeosynclines was thus derived by cannibalism of but slightly older deposits together with frequent additions of new igneous materials, although Kuenen (1958) believes that contributions from large river systems draining vast cratonic regions were also required to "fill" the great geosynclines.

Evidence from the Cordilleran geosyncline illustrates well the concept of continuous, shifting diastrophism so clearly stated by Gilluly in 1949. In fact for much of the Cordilleran region, no single orogenic pulse stands out *clearly* above all others in magnitude between late Paleozoic and early Cenozoic. Recognition of the important late Mississippian-early Pennsylvanian Antler orogeny in western and central Nevada and a medial Permian disturbance of uncertain magnitude in western Nevada (Roberts, 1951; Roberts and others, 1958) were major contributions to Cordilleran knowledge. The wide extent of late Permian volcanism from California to Alaska, clearly indicative of crustal unrest, was realized by Wheeler (1940) and Eardley (1947). Early Jurassic (pre-"Nevadan") disturbances have been recorded by Luper in Oregon (1941), by Ferguson and Muller in Nevada (1949), and in British Columbia by Lees (1936), Little (1949), and Duffell and McTaggart (1952). Finally, radioactive age determinations of granitic rocks long considered classic Nevadan (late Jurassic) indicate that plutonic activity extended from late Jurassic into late Cretaceous and Tertiary (Beveridge and Folinsbee, 1956; Curtis, Evernden, and Lipson, 1958; Larsen and others, 1958; Baadesgaard, Folinsbee, and Lipson, 1959). Geologic field evidence confirms variable batholithic dates in such widely scattered areas as Baja California (Bose and Wittich, 1913), Klamath Mountains (Anderson, 1938), southern British Columbia (Smith and Stevenson, 1955), and northern British Columbia (Aitken, 1955a, b; Kerr, 1932). Willden (1958) has presented other evidence of Cretaceous orogeny in northwest Nevada as well. And, of course, intense diastrophism has continued throughout the Cenozoic.

To this growing list can be added yet another, moderately long episode of tectonism which undoubtedly represents *many local pulses of variable age* within the total time span. Evaluation of available data points to latest Per-

mian and earlier Triassic¹ diastrophism in the Cordillera, the total extent and importance of which has not been fully discussed in literature heretofore. Particularly significant is the presence of widely scattered pre-late Triassic ultrabasic to acidic intrusions in a belt where all such rocks commonly have been considered of Jurassic or Cretaceous age until recent years.

EARLIER REFERENCES TO PERMO-TRIASSIC DIASTROPHISM

That Lower and Middle Triassic are seemingly not represented in most of British Columbia and Alaska was observed early in the century by many geologists. Only in recent years, however, has it been suggested that this apparent hiatus might represent an important, widespread episode of diastrophism, possibly even of mountain building. Ferguson and Muller (1949) describe one or more periods of folding during early or medial Triassic in southwestern Nevada, and Ferguson, Muller, and Roberts (1951) report a significant disconformity at the base of Lower Triassic in northwest Nevada. Eardley (1951), in synthesizing regional tectonic data, concluded that significant Triassic crustal movements must have occurred farther north as well. Kay (1951) briefly summarized Triassic stratigraphy, particularly emphasizing occurrences of conglomerates with plutonic pebbles, as had Schofield earlier (1941). Kay also noted apparent variability in age of ultrabasic intrusions and resultant complications in drawing analogies with modern island arcs. McLearn (1953) noted the probability of widespread pre-Upper Triassic disconformity in British Columbia, and Wheeler (1958) briefly mentioned the westwardly transgressive character of the Triassic across the geosyncline in Nevada and California. White, in a paper presented at the 1958 annual meetings of the American Association of Petroleum Geologists in Los Angeles, stated that "folding, faulting and widespread ultramafic intrusions occurred" during post-late Permian and pre-late Triassic in British Columbia. He chose the name Cassiar orogeny for this important event from the Cassiar District of that province. He indicated further that this was but one of six major post-Proterozoic orogenies there. As the present paper was first being written, White's compilations were published (1959) with a brief summary of evidence for the Cassiar orogeny.

Although Triassic diastrophism has been suggested before in several publications and has been appreciated by various local workers, its full significance nevertheless is thought to remain largely unknown outside the western Cordillera. A recently published textbook by Clark and Stearns (1960) represents the first allusion in a general reference to lands in much of the northern eugeosyncline during earlier Triassic. No discussion was offered, however, of significant orogeny which produced some of these lands. No mention at all was made of such diastrophism in the recently published Triassic Correlation Chart for the United States (Reeside and others, 1957), and it is only tentatively alluded to in the paleotectonic atlas for the Triassic (McKee and others, 1959, p. 5). Most of the evidence lies buried in a formidable literature of obscure references. Furthermore, several bits of new, conclusive evidence have appeared in recent years. The Permo-Triassic disturbances not only are im-

¹ "Earlier Triassic" is used to distinguish from the early Triassic or Bunter Epoch whenever it is desired to refer collectively to all or part of early and medial Triassic.

portant in understanding local Cordilleran history but also are significant to general concepts of mobile belt development. This paper summarizes evidence of Permo-Triassic diastrophism collected since 1954 by the writer from personal work in California, Oregon, and Washington, and from literature. It extends the probable limits of the disturbances and indicates possible significance in terms of general tectonic concepts. Though syntheses of this sort inevitably possess shortcomings, it is felt that the conclusions are of sufficient importance to merit consideration as a working hypothesis for subsequent investigations in the region so that important new evidence will not be overlooked, as apparently has occurred in the past.

TYPES OF EVIDENCE FOR DIASTROPHISM

In this analysis it has been assumed that major transgressive overlaps, particularly those showing angular discordance, conglomerates with mixed clasts (any fragments of unspecified size range) of older rocks, particularly plutonic ones, regional metamorphism, and other evidence of extensive volcanic and plutonic igneous activity indicate some degree of diastrophism, be it merely broad epeirogenic warping or truly orogenic. *Diastrophism* is employed to avoid specific implication of strong horizontal compression versus broad vertical stresses, knowledge of which is connoted by usage of either of the latter terms. Special note is made of ultrabasic intrusions and their alteration product serpentinite. The several possible origins of these rocks present obstacles to tectonic interpretation. A few have formed by local alteration of basic lavas and obviously have different tectonic implications than those formed by alteration of peridotite and related rocks. Hess has emphasized difficulty of dating ultrabasic bodies accurately because of possible tectonic movement after initial emplacement. The writer is convinced that many if not most serpentinites which he has seen have so moved. Inexact dating of sparsely fossiliferous and badly deformed surrounding rocks further confounds interpretation. Plutonic clasts in younger, fossiliferous sediments provides the most satisfactory upper limit, whereas clearly unshaped boundaries with a host rock provide a somewhat less precise lower limit. Certain important ultrabasic masses, such as those of the Cascade Range, Washington, are not discussed because their ages are not satisfactorily established in published sources. They are therefore irrelevant because the objective here is merely to indicate that some important serpentinites of the Cordillera are pre-late Triassic.

The evidence is documented in some detail in the appendix for benefit of the interested reader, but for greater ease of reading is summarized below and in table 1. Only definitive evidence deemed pertinent to proof of pre-late Triassic diastrophism is discussed; no attempt is made to rationalize every fragment of data.

SUMMARY OF EVIDENCE

Evidence for Permo-Triassic diastrophism can be summarized as follows: (1) Unusually extensive late Permian (and probably early Triassic) volcanism, indicating a prelude of crustal instability; (2) Complete lack of recognized Lower and Middle Triassic from Oregon to the Alaska Peninsula together with apparent widespread and abrupt transgression by Upper Triassic

in the same belt (known Lower and Middle Triassic marine sediments are virtually confined to the miogeosyncline north of California and Nevada, fig. 1); (3) Scattered bona fide angular unconformities and widespread discordances together with, at least locally, lesser metamorphism and discordant structures in Upper Triassic rocks; (4) A variety of clast types of underlying older rocks in basal Upper Triassic conglomerates above major unconformities including ultrabasic to granitic, volcanic, and fossiliferous sedimentary constituents; (5) Cross-cutting relations of plutonic igneous bodies with Permian and older rocks.

Negative evidence includes apparent conformity (concordance) of Permian and Upper Triassic in many areas, and presence between fossiliferous

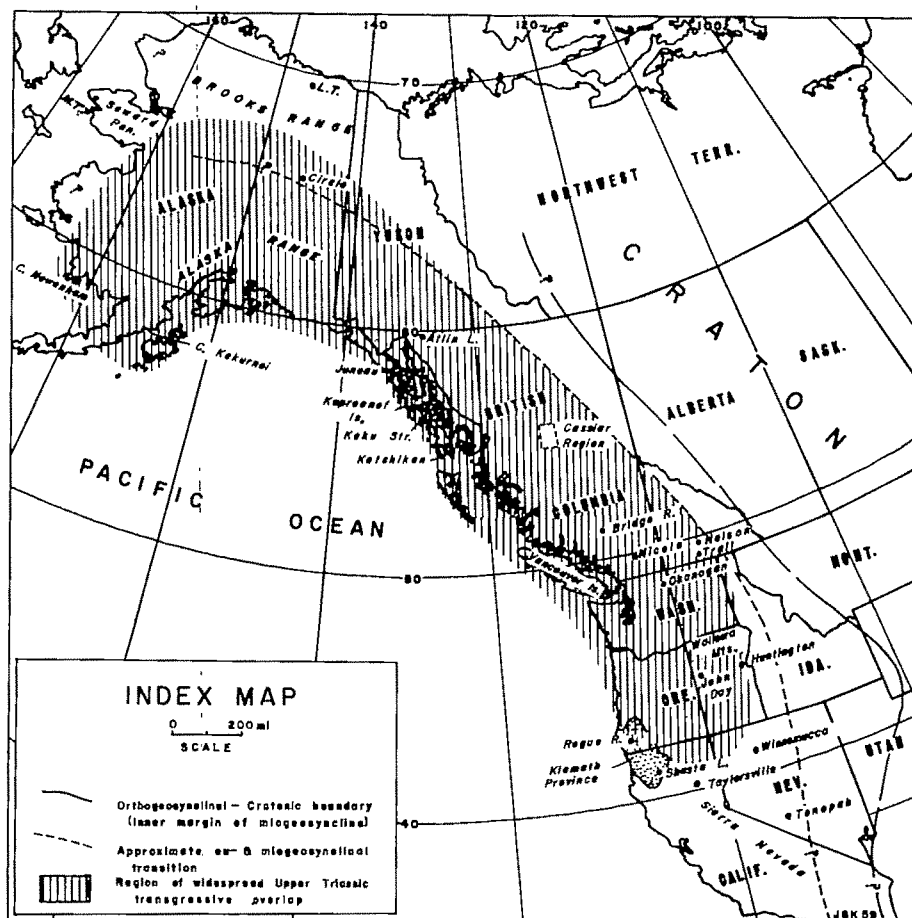


Fig. 1. Index map of principal localities discussed. Note apparent relation of the great region of Upper Triassic transgression to the mio- and eugeosynclinal portions of the northern Cordilleran geosyncline. This region also lacks clearly dated Lower and Middle Triassic, though unfossiliferous volcanics in the eugeosyncline may be in part earlier Triassic.

TABLE 1

Localities	Evidence	References
ALASKA: Southwest*	Angular unconformity between medial Permian (?) volcanics and Upper Triassic limestone	Hanson (1957)
East-Central*	Upper Triassic shale disconformable upon Upper Paleozoic limestone	Martin (1916, 1926), Mertie (1937), Smith (1939)
Southeast (Archipelago)*	Angular unconformity between Upper Triassic and Devonian through Permian; abundant Paleozoic clasts in Upper Triassic conglomerates; local thick volcanics in Triassic	Buddington and Chapin (1929), Chapin (1916)
YUKON: Southwest*	Upper Triassic unconformably overlaps Permian (and earlier Triassic ?) volcanics and sediments and pre-Permian crystalline complex, and contains boulders of plutonic rocks, schist and metavolcanics; serpentinite post-Permian, possibly pre-Upper Triassic	Bostock (1936, 1957), Bostock and Lees (1938), Lees (1936), Tozer (1958), Wheeler (1952)
BRITISH COLUMBIA: Northwest*	Angular unconformity between Upper Triassic and Permian and older rocks, abundant Permian debris in Triassic conglomerates; pre-Triassic plutonic rocks reported as well as post-Permian, pre-Upper Triassic serpentinite	Aitken (1955a, b), Kerr (1932), Schofield (1941), Watson and Mathews (1944)
Central*	Serpentinite and Permian fragments in Upper Triassic conglomerate; serpentinite cuts Middle Permian; widespread unconformity beneath Upper Triassic; volcanics in Permian and Triassic	Armstrong (1949), Hanson (1926), Kerr (1946a, b), Little (1949), Lord (1948), White (1959)
South*	Upper Triassic overlaps Permian and older rocks; conglomerates contain Permian and granitic debris; locally Upper Triassic (?) conglomerate contains serpentinite pebbles, however serpentinite here cuts post-Triassic also; Permian and Triassic contain thick volcanics	Cairnes (1924, 1934, 1937), Cockfield (1948), Drysdale (1917), Duffell and McTaggart (1952), Leech (1953), McCann (1922), Rice (1947), Walker (1934)
VANCOUVER AND SAN JUAN ISLANDS*	Upper Triassic inferred unconformable on Permian (and older) metasediments, volcanics, and serpentinite; Devonian, Permian and granitic clasts in Triassic; thick Permian and Triassic volcanics	Clapp (1917), Gunning (1930), McClellan (1927), McConnell (1914), Mathews (1947), Sargent (1941), Stevenson (1945)

TABLE 1 (Continued)

Localities	Evidence	References
WASHINGTON: North-Central*	Possible unconformity between Triassic and an older metamorphic complex; ultrabasic intrusions cut pre-Triassic, but are not in contact with Triassic	Waters and Krauskopf (1941)
OREGON: Northeast*	Disconformable overlap of Upper Triassic onto older volcanics and metasediments; volcanic and granitic debris in Triassic conglomerates	Beeson (1955), Laudon (1956), Smith and Allen (1941), personal observations
Central*	Widespread angular unconformity between Upper Triassic and Paleozoic sedimentary, volcanic and plutonic complex; Triassic conglomerates contain serpentinite, granitic and Permian fragments; apparent discordance of pre- and post-Triassic trends	Bowers (1953), Lapher (1941), Merriam and Berthiaume (1943), Thayer (1956a,b), personal observations
IDAHO: Western*	Probable disconformity between Upper Triassic and older, partly Permian volcanics; ultrabasic intrusions possibly pre-late Triassic; some volcanics in Upper Triassic	Anderson (1930), Cook (1954), Hamilton (1958), Ross (1938), personal observations
NEVADA: Northwest	Disconformity and local angular unconformity between Permian and Triassic, and between Middle and Upper Triassic; volcanics in Upper Triassic	Ferguson, et al (1951), Roberts, et al (1958)
Southwest	Angular unconformity at base of Upper Triassic and base of Middle Triassic; Upper Triassic locally overlaps Permian; volcanics in Upper Triassic	Ferguson and Muller (1949)
SOUTHWEST OREGON AND NORTHWEST CALIFORNIA: (Klamath Province)	Possible disconformity between Middle Triassic and Middle Permian; ultrabasic masses cut Jurassic strata	Maxson (1933), Rynearson and Smith (1940), Shenon (1933), Thompson, et al (1946), Wells and Walker (1953), Wheeler (1940), personal observations

* In addition to specific evidence cited, all except Nevada and California localities lack definitely recognized Lower and Middle Triassic which further suggests a widespread hiatus.

units of thick, unfossiliferous volcanic and minor sedimentary sequences which apparently are in part of early or medial Triassic age.

Roberts and others (1958, p. 2849) note possible early Triassic ammonites within the Koipato volcanics of western Nevada, heretofore considered wholly Permian (Wheeler, 1940). These volcanics are, however, overlain disconformably by Lower and Middle Triassic sediments in the same region clearly indicating intra-Triassic disturbances. Triassic fossils also have recently been reported in the presumably similar Seven Devil's volcanics of western Idaho (Cook, 1954). An unconformity is inferred in this region between these and Upper Triassic rocks, but the difficulty of determining relationships between thick sequences that have been deformed several times is obvious. Local proof even of angular unconformity does not in itself establish regional extent of such a sharp discontinuity. Furthermore, neither orogeny nor volcanism need necessarily always have raised large areas high enough above sealevel to produce obvious unconformities and clastic wedges. On the other hand, varying volumes of simultaneous sedimentation or volcanism from place to place can have produced quite different stratigraphies in spite of generally similar tectonism. Consequently, geologic records of diastrophism are inevitably variable and obscure.

Although it is tempting to conclude that the whole eugeosyncline from northern California to southwest Alaska was disturbed and elevated, present evidence hardly justifies such a sweeping contention except as mere opinion. A conservative interpretation is that, during the Permo-Triassic orogenies, both tectonic and volcanic lands were raised intermittently within the eugeosyncline by diastrophism with attendant ultrabasic and more acidic igneous plutonic activity in such places as eastern Oregon, southwest British Columbia, and probably parts of Alaska. While these areas were being strongly deformed, the remainder of the belt may have received more or less continuous accumulation of volcanics or possibly have suffered broad warping with development of subtle disconformities.

The writer suggests as a *working hypothesis* that the rate of Permian sedimentary and volcanic accumulation exceeded subsidence and so built up to or slightly above sealevel by early Triassic. Important pyroclastic deposits such as occur in the Snake River Gorge near Homestead, Oregon suggest presence of some volcanic islands, and there may have been very extensive lands during the Triassic. Isostatic adjustment to this volcanic pile by slow subsidence lagged until late Triassic when volcanism had diminished somewhat. The belt then again subsided more uniformly beneath sealevel, or sealevel rose eustatically allowing widespread shallow marine transgression. This resulted in the greatest limestone development in the history of the western eugeosyncline. Some reefs apparently developed on volcanic islands or banks.²

² Organic reefs have been interpreted in the Upper Triassic from Nevada to Alaska for many years (Smith, 1912; Shimer, 1926; Muller, 1936; Bostock and Lees, 1938; Tozer, 1958), apparently on the basis of mere presence of corals. Muller cited more conclusive evidence in Nevada, however. The writer has examined some examples reported in California and Oregon. That in the southern Willows Mountains, Oregon (Smith, 1912) is particularly convincing by virtue of characteristic richly fossiliferous fabric and extreme limestone purity. Squires (1956) interpreted late Triassic coral bank deposits in western Idaho.

This abundance of limestone in the volcanic belt, intimately associated with volcanic rocks, emphasizes the ambiguity of distinguishing eugeosynclinal and miogeosynclinal provinces *primarily* upon the basis of sediment types rather than on presence or absence of volcanics (Kay, 1951, p. 70-71, 88-90; Dott, 1958). Wide transgression and extensive limestone deposition throughout late Triassic time seem compatible with broad, regional down-warping. Simultaneous westward offlap of marine deposits from the craton and miogeosyncline farther east during late Triassic also suggest large-scale epeirogenic warping, perhaps accompanying very extensive isostatic adjustments.

Evidence of regional *disconformities* in eugeosynclines is increasingly recognized, and the writer believes that epeirogenic behavior was also important during Triassic. The interpretation of Triassic history of the northern Cordilleran geosyncline as presented here tends to support suggestion by Hsu (1958) of isostasy as a principal contributor to geosynclinal subsidence patterns. The normal cycle envisioned by him progresses from deep marine to shallow marine and some nonmarine deposits which may or may not include volcanics. Such a sequence should occur where filling of an isostatically adjusting or adjusted depositional basin was complete. The Upper Paleozoic and Triassic of the Cordillera might represent a case in which filling, predominantly by Permian volcanism, progressed more rapidly than did subsidence due to isostatic adjustment after Carboniferous disturbances, thus producing an earlier Triassic hiatus of unknown extent and duration. Prior to or just after the adjustment in earlier Triassic time, certain parts of the belt, if not most of it, were deformed again orogenically, and some areas were invaded by suites of intermediate to ultrabasic igneous rocks. Recurring local instability caused some late Triassic volcanism in British Columbia, southwest Yukon, southeast Alaska, western Idaho and adjacent Oregon, and western Nevada. Severe orogeny best explains igneous intrusions and angular unconformities in southern Alaska, central British Columbia, and eastern Oregon. Epeirogeny (or eustatic rise of sealevel) may better explain concordance and disconformity in northern Alaska, southern British Columbia, Snake River gorge, and possibly northern California. Relative timing of the two processes can not now be judged.

TECTONIC CONCLUSIONS

The venerable concept of simple, long-continued subsidence of geosynclines terminated by one great "revolution" is now generally regarded as untenable by students of orogenic belts. Multiple or essentially continuous orogeny and epeirogeny of varying intensity throughout the history of mobile belts with tectonic and volcanic lands being raised, eroded and re-elevated—sometimes in the same positions, sometimes not—at varying times along and across the belts are clearly indicated. And the complexity of western Canada, thought by White (1959) to be atypical of the North American Cordillera, is regarded by the present writer as very *typical* of mobile belts, although *any* generalization about such provinces is hazardous.³ There is every reason to believe that areas both to the north and south are equally complex.

³ Apparent narrowness of the belt in British Columbia (600 miles) and Alaska (700 miles) may well be more normal than the wide sector across California, Nevada and Utah (900 miles).

All manifestations of diastrophism, e.g. warping, folding, batholithic development, and regional metamorphism, show considerable age variation along as well as across orogenic belts. It is now established from several different lines of evidence that the granitic batholiths of the Cordillera vary greatly in age; therefore similar variation of the ultrabasic rock bodies may be expected intuitively. Hess (1955, fig. 4) has indicated longitudinal variation of ultrabasic rock ages in the Cordillera on a very large scale but implies that it would not be expected more locally. He shows three separate, parallel belts of ultrabasic rocks, all of different age as follows: late Triassic (Oregon-central British Columbia-northern Alaska), Jurassic (California), and Cretaceous (southeastern Alaska). The "late Triassic" belt has been shown subsequently to include considerable post-medial Permian and pre-late Triassic ultrabasic rocks, and in fact White (1959) assigned all British Columbia examples to this age (his Cassiar orogeny). Review of original descriptive sources with critical evidence bearing upon serpentinite dates reveals that several different ages exist even in the same belt, notably in British Columbia, where they appear to vary from at least Permo-Triassic to Cretaceous.

Because serpentinites have been for many years thought to mark axial zones of mobile belts and to have been intruded at only one time in a given belt, namely, when the geosyncline first was severely deformed (Hess, 1939, 1955), proof of multiple ages is to the point. Hess (1955) has suggested that a *single* serpentinite date marks initial mountain building for distances of as much as 1000 miles along the strike of a mobile belt. A Jurassic age was long assumed throughout the Cordilleran belt, apparently as a corollary to the general premise that virtually all the large western batholiths and severe orogenesis were late Jurassic ("Nevadan"). Although the latter phenomena have since proved repeatedly to span almost the whole history of the geosyncline, adjustment of age assignments of ultrabasic rocks has lagged. Lupper (1941) first presented evidence of pre-Jurassic serpentinite in central Oregon, but only in the past decade has accumulating data indicated decisively that much of this serpentinite as well as other important plutonic igneous activity and regional metamorphism in the northern Cordillera were *pre-late Triassic*. In eastern Oregon, at least, Permo-Triassic orogenies were much more important than were classic late Mesozoic or "Nevadan" deformations.

In the writer's opinion, it is primarily the obscurity of the more ancient rock record and our limited ability to read it that has given past impressions of regular, unbroken progression from simplicity to increasing complexity in mobile belts. Even the age of such renowned events as the Nevadan revolution in western United States and supposedly equivalent Coast Range orogeny in British Columbia and Alaska are now known to be so variable as to make the terms meaningless without careful definition for any given locality. Their usefulness has been seriously questioned by other workers, notably Peter Misch (personal communication), as well as by the present writer. Ironically, there is only one small area in California in the southern Klamath Mountains (outside the Sierra Nevada Mountains whence the name Nevadan derived) where truly classic Nevadan, i.e. intra-late Jurassic, deformation and batholithic emplacement can be dated positively by geologic field evidence and radiochemical

data (see Appendix). Many of the larger California batholiths and attendant orogenesis date from the late Cretaceous (Santa Lucian orogeny), therefore the longstanding term "Nevadan revolution" is grossly misleading unless extended to include *all late Mesozoic diastrophism* or restricted to encompass only this one brief and local part of that diastrophic interval as suggested by Curtis, Evernden, and Lipson (1958).

Late Mesozoic diastrophism not only was variable in age *along* the mobile belt but apparently merged rather insensibly *eastward* (cratonward) with the supposedly younger Laramian orogeny.⁴ This is particularly true in intermediate areas, such as the Great Basin and central British Columbia, where there is also evidence of intermediate Cretaceous as well as older and younger deformation and plutonic activity (Smith and Stevenson, 1955; Willden, 1958).

Demonstration of extensive orogenic and epeirogenic disturbances of the first order during late Permian and earlier Triassic time in at least the northern Cordillera indicates essential continuity of tectonic unrest at least from late Paleozoic through Mesozoic into Cenozoic time. It is axiomatic that choice of any one orogenic pulse as most fundamental in this region becomes exceedingly difficult. Emplacement of immense batholiths would seem the most profound event, but even this spanned considerable time. As a corollary it is suggested that naming and attempted correlation of minor orogenic pulses is even more suspect, and plea is voiced for complete purging of the still-extant textbook creed of an oversimplified and universal *geosynclinal cycle*. It has little basis in fact if the Cordilleran geosyncline be accepted as a significant example.

APPENDIX

GEOGRAPHIC TABULATION OF EVIDENCE OF PERMO-TRIASSIC DIASTROPHISM

Alaska.—With the exception of recently discovered Lower and Middle Triassic in northern Alaska (Reeside and others, 1957) and one poorly documented Middle Triassic locality on Seward Peninsula, only the Upper Series of the Triassic is recognized (Martin, 1916). This Series blanketed virtually the whole state and includes some of the most fossiliferous and readily recognized strata. In the Alaska Range they are reportedly disconformable upon Upper Paleozoic sediments (Martin, 1916, 1926; Smith, 1939). Near the Yukon border ultrabasic rocks intrude Devonian and have been considered of pre-Mississippian age (Mertie, 1937; Smith, 1939). But they could as well be much younger since they are not in contact with post-Devonian rocks other than granites. Payne (1955) reports ultrabasic intrusions in the western Brooks Range and on Seward Peninsula and refers them to "Jurassic orogenies." Ultrabasic rocks have intruded Paleozoic and possibly Mesozoic meta-

⁴ This condition seemingly is inconsistent with simple accretion of mobile belts outward from continental nuclei (cratons). Misch, lecturing in 1954 on Cordilleran Structure, pointed out the anomalous character of the central and southern Rocky Mountains in that they are the only very high mountains lying *outside* of orthogeosynclinal belts and apparently lacking great batholithic roots (other than discordant Precambrian granites). Too much tectonic significance may have been attached to the Rocky Mountains in terms of normal continental growth and framework if they are truly so atypical. Seismic evidence suggests thicker crust beneath the Rockies (47 km) than the Plains (35-41 km), which would be expected if the mountains approach isostatic compensation (Ewing and Press, 1959). Geologic explanation of such thickening remains to be clarified, however.

sediments and volcanics in southwest Alaska at Goodnews Bay near Cape Newenham (Harrington, 1921). These intrusions are considered Tertiary on the new geologic map of Alaska (published 1958). Hess (1955) considered all of the above ultrabasics to be late Triassic. Conclusive evidence of age seemingly has not yet been found.

In and south of the Alaska Range, Upper Triassic generally overlies thick volcanics which at numerous localities contain or overlie Permian fossiliferous sediments (Hanson, 1957; Martin, 1916, 1926; Smith, 1939). At only a few places is there definite evidence of significant folding and unconformity. At Cape Kekurnoi on the Alaska Peninsula, Hanson (1957) reports an angular unconformity between probable Permian agglomerates and Upper Triassic strata. Ultrabasic intrusions are not reported on the Alaska Peninsula, but those further northeast on Kenai Peninsula have been generally referred with little evidence to the "Jurassic orogenies" of Payne (1955).

In the southeastern Alaska archipelago, there is compelling evidence of earlier Triassic diastrophism. In the Ketchikan area Upper Triassic overlaps Upper Paleozoic and Devonian rocks and contains angular Devonian and coarse granite clasts (Chapin, 1918). The same relationship exists elsewhere, as at Keku Strait (Buddington and Chapin, 1929), where Upper Triassic overlaps Devonian and Permian again with abundant clasts of each incorporated in the Triassic. The Upper Triassic here contains notably thick lavas as it does at Juneau. Elsewhere in the archipelago the Upper Triassic generally rests upon Permian greenstone or Permian sediments and has widespread conglomerates containing abundant Permian clasts (Buddington and Chapin, 1929).

Ultrabasic intrusions occur throughout the archipelago in a belt at least 100 miles wide and parallel to the west margin of the Coast Range batholith of British Columbia. Locally they are cut by granitic dikes and long have been assumed to be late Jurassic or Cretaceous (Buddington and Chapin, 1929). Such dating seemingly has been based only upon analogy with the Sierra Nevada, California (Knopf, 1929; Taliaferro, 1943) and assumption that ultrabasic intrusions immediately preceded batholithic development. Larsen and others (1958) determined a mean age of 105 ± 13 million years (medial Cretaceous) for 16 samples of the Coast Range batholith complex from Washington to southeast Alaska, and this age has apparently been regarded as representing the last major activity. But the batholith is composite and several younger plutons are known in British Columbia (Baadesgaard, Folinsbee, and Lipson, 1959). Hess (1955) has referred all of the ultrabasic masses of southeast Alaska to the Cretaceous. At a few localities they appear to intrude Cretaceous strata (Kennedy and Walton, 1946; Rucknick and Noble, 1959), but there is no really satisfactory published evidence of their ages in the whole archipelago.

As early as 1916 Martin favored interpretation of widespread uplift in late Permian time throughout Alaska and nondeposition of Lower and Middle Triassic, resulting in a significant hiatus. He admitted, however, that thick, unfossiliferous greenstones beneath the proven Triassic at many localities could be of earlier Triassic age in part, and, therefore, conformable. Permo-Triassic orogeny is indicated in the archipelago and probably also at Cape Kekurnoi;

epeirogeny or eustatic rise of sealevel is evident in central Alaska, and may have been very extensive.

Yukon and Northwest British Columbia.—Upper Triassic rocks are known in southwestern Yukon where they overlap Permian sediments and volcanics as well as the Precambrian or Paleozoic Yukon complex of metamorphic and Plutonic rocks (Bostock, 1936, 1957; Lees, 1936; Tozer, 1958; Wheeler, 1952). Serpentinite in this region cuts the Yukon rocks and the Permian, and is cut by Jurassic or Cretaceous granite (Bostock and Lees, 1938; Watson and Mathews, 1944). Lees (1936) and Wheeler (1952) state that "serpentinite" appears to cut Jurassic rocks. Relationships are too poorly known to allow confident dating of the Yukon ultrabasics; however, on the border of northwestern British Columbia at Atlin Lake, serpentinite was recently dated as post-Permian and pre-Triassic by Aitken (1955b). J. O. Wheeler and Tozer postulate Triassic as well as Permian volcanism. Presumably, a volcanic arc in southwestern Yukon and southeastern Alaska contributed lavas and pyroclastics through much of Permian and Triassic time. Limestone reefs developed in late Triassic (Tozer, 1958). Upper Triassic is known in northwest Yukon but lacks volcanics (Martin, 1959) and is here considered miogeosynclinal, akin to east-central Alaska.

Throughout northwest British Columbia, Upper Triassic rests with angular discordance upon Permian and older rocks and contains abundant Permian clasts as it does in Yukon and adjacent southeast Alaska. Pre-Triassic plutonics are reported by Kerr (1932), Aitken (1955a, b), and Schofield (1941); however the first abundant granitic debris occurs in Jurassic sediments (Bostock and Lees, 1938; Kerr, 1948a, b). Lower and Middle Triassic are known definitely only in the nonvolcanic (miogeosynclinal) belt of northeast British Columbia (fig. 1).

Central British Columbia.—The Cassiar District (a geographic subdivision lying north of 55° north latitude) contains the most conclusive evidence for pre-Upper Triassic ultrabasic intrusions. At Pinchi Lake, serpentinite pebbles have been found in Upper Triassic conglomerate, and the ultrabasics have intruded medial Permian and older rocks (Armstrong, 1949; Little, 1949). The conglomerates also contain abundant Permian clasts, and a significant unconformity is inferred between the Permian and Triassic (Armstrong, 1949). Upper Triassic sediments and volcanics rest upon Permian widely in surrounding areas also, and contain Permian clasts (Hanson, 1926; Kerr, 1948a, b; Lord, 1948). Post-Permian and pre-Cretaceous acidic dikes are reported which could be earlier Triassic (Armstrong, 1949). Presumably White (1959) had in mind the above evidence when he chose the name Cassiar for Permo-Triassic orogeny in British Columbia. In addition, he states (p. 72) that fold trends and metamorphism vary markedly between Upper Paleozoic and Mesozoic rocks in several areas, though such evidence was not encountered in other literature.

It is particularly important to note that younger, probably Jurassic and Cretaceous, ultrabasic intrusions are also reported in this region. Lord (1948) found that in the nearby McConnell Creek area ultrabasics probably intruded

Upper Triassic or Lower Jurassic sediments and that clasts of "serpentine" occur in Upper Cretaceous conglomerates.

Southern British Columbia.—Permian and Upper Triassic sediments and volcanics have been known for years in southern British Columbia; however, their relations to each other and to various plutonic rocks are still not clearly established.

West of the Fraser River in the Bridge River-Shulaps-Tyaughton area of the eastern Coast Range, McCann (1922) reported Upper Triassic conglomerates with "serpentine" clasts, seemingly conclusive evidence of pre-late Triassic ultrabasic intrusions, together with granitic and Permian sedimentary debris. This observation was not mentioned by subsequent workers (Cairnes 1937; Leech, 1953) who considered the same intrusions to be younger, probably Jurassic. Leech (1953) believes that they are intra-late Triassic. He states that they cut Triassic and are overlapped by Lower Jurassic fossiliferous sediments containing detrital chromite, presumably derived from unroofed serpentinite. Locally the Jurassic seems also to be cut by serpentinite, but Leech believes this to reflect remobilization by plastic flow as "tectonic intrusions" during later folding. If this be true, then perchance intrusive relations with Triassic rocks had a similar tectonic origin, making original emplacement pre-late Triassic. This would be consistent with McCann's report of "serpentine" pebbles in Triassic.

East of the Fraser River in the Nicola and adjacent map areas, Upper Triassic rests upon Permian deposits of varying character, and Triassic conglomerates contain Permian and granitic clasts (Cockfield, 1948). Serpentinite reportedly cuts Triassic rocks and was unroofed to furnish detritus to late-early Cretaceous conglomerates (Cairnes, 1924; Cockfield, 1948; Crickmay, 1930; Duffell and McTaggart, 1952; Rice, 1947). Pre-early Cretaceous granodiorite cuts the serpentinite (Rice, 1947). At least some of the granitic bodies in this part of British Columbia are post-Triassic and pre-Middle Jurassic (Cockfield, 1948; Duffell and McTaggart, 1952), though others are still younger (Baadesgaard, Folinsbee, and Lipson, 1959). Throughout this region the ultrabasic intrusions are generally considered of Jurassic age on what appears to be incomplete evidence, though possibility of remobilization tectonically is mentioned for serpentinite in a fault zone along the Fraser River (Duffell and McTaggart, 1952), implying a possible older true age. Presence of Jurassic and younger ultrabasic intrusions in this region was not mentioned by Hess (1955) or White (1959).

In southeast British Columbia, Upper Triassic rests principally upon Precambrian-early Paleozoic Windermere metamorphics as well as doubtful Permian (Cairnes, 1934; Drysdale, 1917; Walker, 1934). A considerable pre-late Triassic hiatus and late Triassic transgression is indicated. Peridotite in the Trail-Nelson area cuts the Windermere or older rocks but is not in contact with Triassic (Rice, 1947), rendering accurate dating impossible.

Vancouver Island.—Vancouver Island contains widespread Triassic, with only Upper Triassic recognized (summarized by McLearn, 1953). It overlies thick sediments and volcanics which are at least in part Permian (Gunning, 1930; Sargent, 1941; Stevenson, 1945). Widespread lithologically similar but

unfossiliferous metamorphic rocks are generally considered to be equivalent (Clapp, 1917; Mathews, 1947). Unfaulted relationships between the Upper Triassic-Lower Jurassic Vancouver group (sediments and volcanics) and older rocks have never been observed, but an unconformity is inferred (Clapp, 1917), presumably because of contrasting degrees of disturbance. This conclusion is tenuous, however, because of structural complexity of a monotonous sequence. Angular unconformity at the base of Upper Triassic is inferred on nearby Texada Island (McConnell, 1914); however, relationships are obscure there also.

Washington.—The San Juan Islands, adjacent to the southeast end of Vancouver Island, contain metavolcanics and sediments with late Permian fusulinids (Thompson, Wheeler, and Danner, 1950). These were correlated in part with the Vancouver Island Upper Paleozoic rocks by McClellan (1927), and were said to be intruded by ultrabasic bodies. Upper Triassic sediments with clasts of Devonian and Permian as well as granitic material occur on one island, but are completely isolated from the older sediments and ultrabasic intrusions so that stratigraphic relations can only be inferred. McClellan (1927) believed that diastrophism and intrusions preceded Upper Triassic deposition.

The only other known *pertinent* Triassic locality in Washington is in the Okanogan Valley east of the Cascade Mountains. Waters and Krauskopf (1941) discovered Triassic fossiliferous limestone resting on deformed meta-sediments and greenstone of the Anarchist series (in part Permian). Basal Triassic conglomerate contains rounded clasts of Anarchist lithologies, suggesting a possible erosional interval between. None of the strata were well dated, and though ultrabasic intrusions occur within the Anarchist, they are not in contact with Triassic. Important ultrabasic rocks in the Cascade Range, notably the Mount Stuart body, are too poorly dated to provide evidence pertinent to Permo-Triassic diastrophism.

Eastern Oregon and western Idaho.—Though absence of Lower and Middle Triassic was recognized early in Alaska and British Columbia, the Triassic of Oregon, Washington, and Idaho remained poorly known. On the basis of extended recent mapping and dating of the rocks, only Upper Triassic is recognized. It is, of course, likely that some of the thick volcanic sequences generally referred to the Permian (Wheeler, 1940) may include some earlier Triassic as well (Cook, 1954).

Lupher (1941) concluded that serpentinite in central Oregon cut Triassic sediments and was overlain by Jurassic. Recent important work by the U. S. Geological Survey (Thayer, 1956a, b), however, has shown that serpentinite detritus is present in basal Upper Triassic sediments, indicating a pre-late Triassic age. Such detritus was also found in thin sections in 1955 by P. H. Masson, then of Humble Oil and Refining Company, in sediments studied by Masson and the writer in the Aldrich Mountains. Thayer believes that some of the serpentinite bodies were mobilized during subsequent deformation so that they formed plastic "tectonic intrusions" into Triassic rocks locally. He believes that an extensive complex of more acidic igneous rocks and regional metamorphism also dates from earlier Triassic. During 1954 and 1955 the writer

and several colleagues with Humble Oil and Refining Company working in the same area examined Thayer's evidence as well as that in other areas. The writer is in agreement with his interpretations. Serpentinite, gabbro, and diorite all cut metavolcanic rocks and lenses of Permian limestone with fusulinids east and south of John Day, and Upper Triassic conglomerates and sandstones of the area contain clasts of all of these older igneous rocks (Thayer, 1956a, b, and personal communication). Similar volcanics and associated sediments are widespread in eastern Oregon and have been dated as Permian at several other localities (see below). Certainly some, if not all, of the serpentinite of eastern Oregon is pre-late Triassic, and Upper Triassic sediments transgressed a complex basement of deformed Paleozoic sediments and volcanics intruded by varied plutonic rocks. Thayer believes that virtually all of the albite granites of northeastern Oregon are pre-late Triassic (personal communication). Gilluly earlier (1937) suggested that some of these were older than granodiorites around Baker, Oregon. There can be no doubt that this region suffered orogenesis of the first order during early Mesozoic!

Approximately 50 miles southwest of John Day in the vicinity of Suplee, Upper Triassic is closely associated with early Permian and older sediments (Lupher, 1941; Merriam and Berthiaume, 1943), but the later Permian volcanics have been removed by pre-late Triassic erosion or were never deposited there. The writer favors the former interpretation because Permian volcanics were so widespread, being present in virtually every other Permian sequence from California to Alaska (Wheeler, 1940). Furthermore, there is evidence of angular unconformity, and Upper Triassic conglomerates in the area contain abundant volcanic, chert, and mudstone clasts together with Permian fusulinid-bearing limestone and granitic debris. There are also complex north-trending structures in the Paleozoic rocks which appear to be discordant with simpler east-trending ones in younger Mesozoic and Cenozoic strata.

At Mitchell, Oregon, 30 miles northwest of Suplee, Upper Paleozoic meta-sediments with poorly preserved fusulinids and other fossils were deformed, metamorphosed, and intruded by ultrabasic rocks prior to overlap by Cretaceous sediments (Bowers, 1953). Furthermore, north-trending lineations in phyllite were noted by Maason and the writer in 1955, but folds in Cretaceous and Tertiary rocks of this area trend east-northeast as at Suplee. Unfortunately, neither Triassic nor Jurassic strata are present to provide more precise dating of the disturbances, but it is probable that here, too, they date from the pre-late Triassic.

Wheeler (1940) summarized information concerning thick andesitic volcanics in the Wallowa Mountains, along the Snake River gorge, and in western Idaho. He concluded that all were Permian; however, fossil evidence was scant (Anderson, 1930; Gilluly, 1937; Ross, 1938). These rocks are overlain at several localities by widespread Upper Triassic sediments and some contemporaneous local volcanics (Ross, 1938; Cook, 1954). Stratigraphic relationships are commonly obscure, and it is claimed that Triassic fossils occur also in the main mass of supposed Permian volcanics (Cook, 1954; Hamilton, 1958). Unfortunately, none of the fossils or details of stratigraphy of the Idaho sequence have ever been described. Evidence in the Wallowa Mountains and

Snake River gorge of Triassic conglomerate with abundant volcanic and rare granitic clasts (Laudon, 1956), as well as supposed disconformable overlap relations of Upper Triassic units (Smith and Allen, 1941), are taken to indicate at least local, pre-late Triassic hiatus. The very sparsely fossiliferous older greenstone sequence is probably in part Triassic as are the similar Koipato volcanics of western Nevada (Roberts and others, 1958). Therefore Cook's inference (1954) that volcanism and some sedimentation went on more or less simultaneously is accepted. During earlier Triassic, volcanic islands apparently formed in northeastern Oregon and western Idaho, and unconformities developed. Evidence indicates that organic reefs grew around islands and on shallow submarine banks during late Triassic.

In the Elkhorn Mountains northeast of John Day, Oregon, ultrabasic rocks cut Permian fusulinid-bearing strata (Taubeneck, 1955), but no younger sediments directly overlie them to bracket their age. The ultrabasics are themselves cut by younger granitic rocks (Gilluly, 1937), which have been dated as 102 million years by Larsen and others (1958, p. 51). In adjacent western Idaho, Anderson (1930) reported ultrabasic intrusions that may have intruded Triassic, but critical contacts are concealed. Granitic rocks in the area are younger than both ultrabasics and the Triassic (Anderson, 1930; Hamilton, 1958). The Idaho batholith proper, farther east, has been dated from 16 samples as 108 ± 12 million years (medial Cretaceous) by Larsen and others (1958), but it is known to be of composite origin. Eighty miles south at Huntington, Oregon on the Snake River, Beeson (1955) discovered Upper Triassic fossils in shales which unconformably overlie metavolcanic and meta-sedimentary rocks of presumed Paleozoic age.

Southwestern Oregon and northern California.—In the Klamath province of northwestern California and adjacent Oregon, ultrabasic rocks and serpentinite are unusually widespread. They intrude Jurassic sediments and volcanics, and are cut by diorite and quartz diorite (Maxson, 1933; Rynearson and Smith, 1940; Wells and Cater, 1950). The Shasta Bally batholith at the south end of the province has been dated by the potassium-argon method as 134 million years (late Jurassic) by Curtis, Evernden, and Lipson (1958), and as 81 to 112 million years (late Cretaceous) by the lead-alpha method (Larsen and others, 1958). The writer has examined field relationships with overlapping fossiliferous early Cretaceous (Valanginian) sediments, and is convinced that the batholith must be older than the latter determination, i.e. late Jurassic. Significantly, this is the only batholith along the Pacific Coast dated accurately by *both* isotopic and geologic methods that is truly of classic Nevadan (intra-late Jurassic) age. Others in the Klamath region and elsewhere are dated positively only as post-late Jurassic and pre-late Cretaceous on geologic evidence (Shenon, 1933; Wells, 1956; Wells and Walker, 1953).

The widespread affinity of serpentinite for fault zones in the Klamath Province renders intrusive dating extremely difficult. The writer has studied some of this region, and near Rainie Falls in Rogue River Canyon, Oregon, serpentinite was observed which clearly transects Jurassic greenstone in fresh outcrops with knife-sharp contacts and lacks evidence of post-intrusive shearing and brecciation so common elsewhere. In the Kerby Quadrangle ultrabasic

rocks intrude Jurassic metasediments, and serpentinite clasts occur in overlapping Cretaceous sediments (Shenon, 1933).

Supposed Triassic age of the Applegate metasedimentary and metavolcanic "series" of southwest Oregon has become accepted and widely extended. This practice is unjustified, however, for such a complex sequence which contains but one very poor fossil locality. The unit presumably includes rocks of varying ages whose mutual relationships are unknown, therefore no evidence can yet be won from it concerning possible Permo-Triassic diastrophism.

In the Shasta Lake area, California, Middle Triassic is present, resting with apparent concordance upon Middle Permian (Thompson, Wheeler, and Hazzard, 1946). Disconformable overlap seems indicated, because neither Upper Permian nor Lower Triassic are recognized, and the intervening unfossiliferous interval is relatively thin (Wheeler, 1940). A similar relationship is suggested 50 miles southeast at Taylorsville in the northern Sierra Nevada, where Triassic and Permian deposits appeared to the writer to be lithologically very much like those at Lake Shasta. Diller believed the Permian-Triassic contact there to be an angular unconformity, but this is open to serious question in light of the very complex structural relationships and metamorphism in the area (see also Reeside and others, 1957). Ultrabasic intrusions in this vicinity are considered late Jurassic or Cretaceous and pre-batholithic, but without positive local evidence.

In the Mother Lode district of the western Sierra foothills, no Triassic has been identified, although the writer believes that it is probably represented in the Calaveras formation, a catch-all metamorphic unit which has thus far yielded Carboniferous and Permian fossils. Here the ultrabasic rocks are considered late Jurassic, having intruded early-late Jurassic sediments, having been subsequently folded with them, and finally having been cut by western Sierra granodiorites (Knopf, 1929; Taliaferro, 1942). These granitic bodies are considered 131 to 143 million years old (late Jurassic) by Curtis, Evernden, and Lipson (1958) and Larsen and others (1958).

Taliaferro (1943) believed the serpentinites of the Sierras to be latest Jurassic (Kimmeridgian) and "pre-Nevadan," while he considered those of the Coast Ranges to be "post-Nevadan" (Tithonian). The latter reportedly cut "Knoxville" sediments and were folded with them but do not cut Cretaceous and Tertiary except by later plastic, tectonic remobilization. Lower Cretaceous conglomerates contain clasts of "Franciscan" and "Knoxville" lithologies as well as some of the associated intrusives, according to Taliaferro, but it is not clear if *ultrabasic clasts* are included in the conglomerates. In the California Coast Ranges, as in southwest Oregon, serpentinite commonly occurs along fault zones and is intensely sheared. Because they have been remobilized tectonically and the ages of enclosing unfossiliferous sediments are so tenuous, the dating of initial emplacement of the Coast Range ultrabasic intrusions is by no means certain.

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STRATIGRAPHIC AND LITHOLOGIC VARIATIONS IN THE COLUMBIA RIVER BASALT

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ABSTRACT. The Columbia River basalt has been sampled by 28 stratigraphic sections and by the mapping of selected areas.

Petrographically, and also stratigraphically, the rocks assigned to this formation by Merriam, Lindgren, and Smith are divisible into two distinct varieties. The older, widespread in the Imnaha and John Day regions, is characterized by about 5 percent olivine, a silica content of 47 to 50 percent, and by notably higher Al_2O_3 , MgO , and CaO than the younger. Many outcrops have a characteristic "greasy" appearance because of the presence of saponite after olivine and of nontronite and other clay minerals after chlorophaeite. The basalts at Picture Gorge and Turtle Cove, described by Merriam in 1901, are typical.

The younger basalts are characterized by more than 20 percent tachylite, little or no olivine, a silica content of 53 to 54 percent, and by notably greater amounts of K_2O and TiO_2 . Nearly all the basalts that occupy the central and eastern part of the lava field north of the John Day and Imnaha areas are of this kind. They constitute the Yakima basalt as defined by Smith in 1901. In the lower part of the Imnaha River canyon, and also in the John Day basin, the Yakima basalt rests with distinct structural unconformity on flows of the older Picture Gorge type.

A late variant of the Yakima basalt emerged after warping and faulting had started to deform the Yakima flows in early Pliocene time. It contains more olivine and plagioclase and a distinctly higher percentage of iron and titanium than normal Yakima flows.

Because of their separation in time, differences in chemical and mineral composition, and particularly because of the absence of transitional varieties between them, these lithologic and stratigraphic variations of the Columbia River basalt are considered to be products from separate magmatic hearths, and not differentiates of a hypothetical uniform magma.

INTRODUCTION

The name Columbia River basalt was given to the basaltic lavas of the Pacific Northwest by Russell (1901, p. 28). Still earlier Russell (1893, p. 20-22) had described the basalt under the name "Columbia lava," and had noted that its best sections are "in the precipitous walls of the coulees or canyons in Douglas County,¹ and in the remarkable gates eroded by Yakima River through ridges" in the basalt, but he extended the name to include lavas that range in age from Eocene to Recent, and which spread over most of eastern Washington, eastern Oregon, the plains of southern Idaho, and the plateaus of northeastern California.

Merriam (1901, p. 303) held that only one unit of the several included by Russell should retain the formation name, and "This one should be the horizon which is most prominent along the Columbia River." He redefined the Columbia lava as follows: "In the John Day basin it is found that the lavas of the Columbia form a well-defined series which lies between the John Day [Oligocene and Lower Miocene] and the Mascall [Middle to Upper Miocene] formations. . . . This series is, moreover, that one of the several to which the name is applied which has the greatest lateral extent, forming probably the largest lava field of the world." Merriam stated that at Turtle Cove [Kimberly, Grant County, Oregon] 23 flows of basalt can be counted in the bluff.

Simultaneously with Merriam's work in the John Day basin, Smith (1901, p. 15) investigated the Yakima region of central Washington and faced the

¹ At the time Russell wrote, Douglas County, Washington, included the area later split off to form Grant County.

same problem. Here Russell (1900, p. 129-134) had described four "sheets" of basalt flows of different ages as constituting the Columbia River lava. Smith decided it was "inadvisable to use the general formation name, because the lavas of different ages must necessarily be separated" in the detailed mapping of the Yakima area, and he introduced the term *Yakima basalt* for the Miocene flows. The Yakima basalt, he wrote, "includes ten or more flows in the canyon of Yakima River where more than 2,500 feet is exposed in vertical section." Smith also noted that the Yakima basalt includes "flood after flood of molten rock, which covered the vast area between what is now the crest of the Cascade Mountains on the west and the mountains of Idaho on the east, and between the mountains of northeastern Washington and the Blue Mountains of Oregon on the south."

In the same year Lindgren (1901, p. 592), in his report on the gold belt of the Blue Mountains in Oregon, also suggested restricting the term Columbia River lava to basalts of Miocene age.

Although the U. S. Geological Survey (Wilmarth, 1938, p. 495) condoned the use of Columbia River basalt as a "blanket term, covering basalts of Eocene, Miocene, and Pliocene (?) age in the broad region described by

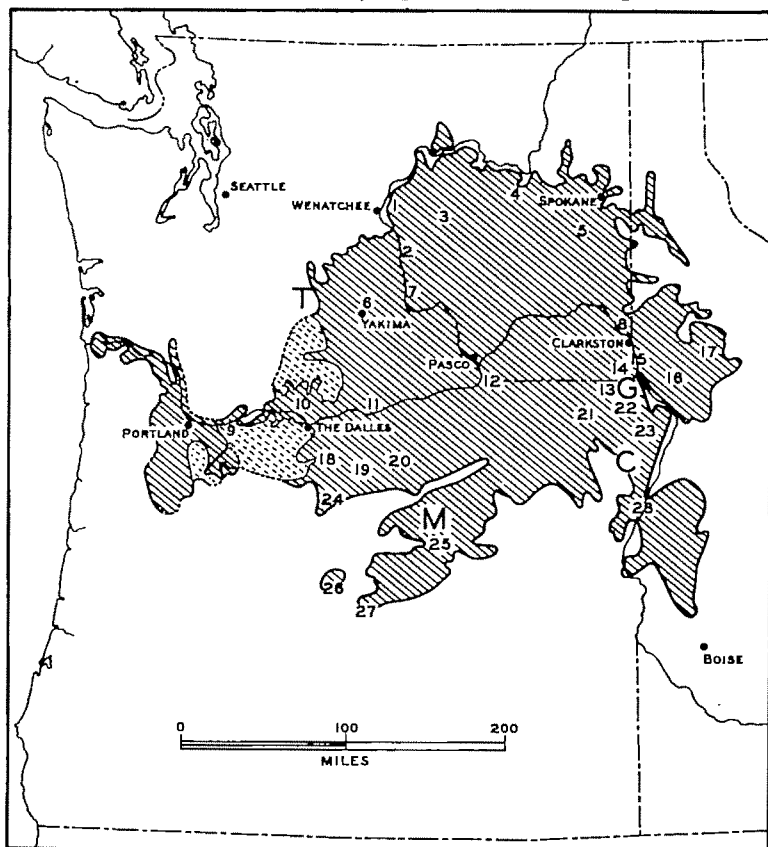


Fig. 1. Columbia River basalt. Area covered by the younger volcanic rocks of the Cascade Mountains is indicated by broken lines.

Russell," nearly all geologists since the time of Merriam, Smith, and Lindgren have restricted it to the dominantly Miocene flows that form the great area of flood basalts outlined in figure 1. In general, the terms Columbia River basalt and Yakima basalt have been used as synonyms, but there has been some tendency in the literature to apply Yakima basalt mainly to the western part of the lava field, particularly to the well-exposed flows along the eastern foothills of the Cascade Mountains. Moreover, the stratigraphic equivalence of the three areas named as "typical": (1) coulees and canyons of Douglas County (Russell), (2) canyon of Yakima River (Smith), and (3) Turtle Cove, John Day basin (Merriam) have never been demonstrated, and the general nature of the individual flows making up this vast assemblage of flood basalts remains little known.

In this paper some stratigraphic relations of the basalts in this vast lava field are summarized, together with data regarding the variation in composition of the basalts regionally, and with time. This summary is based on a sampling of the lava field by 28 measured stratigraphic sections whose locations and thicknesses are given in table 1, and whose positions are indicated in figure 1. Among these sections are the ones regarded as "typical" by Russell (numbers 1, 2, and 3), Smith (number 6), and Merriam (number 25), as well as the much thicker sections in the Columbia Gorge through the Cascade Mountains, and on the walls of the canyons of the Snake, Grande Ronde, Imnaha, and

TABLE 1
Measured partial sections of Columbia River basalt

Section number (plate 1)	Name and Location	Thickness in feet	Number of flows
1.	Waterville-Douglas Creek, Douglas County, Washington	910	10
2.	Crescent Bar, Grant County, Washington	945	10
3.	Dry Falls, Grant County, Washington	450	8
4.	Lincoln, Lincoln County, Washington	330	4
5.	Rock Lake, Whitman County, Washington	250	3
6.	Roza Gap, Yakima County, Washington	845	9
7.	Sentinel Gap, Grant County, Washington	1190	16
8.	Uniontown Plateau, Whitman County, Washington	1735	25
9.	Multnomah Falls, Multnomah County, Oregon	730	8
10.	Klickitat River, Klickitat County, Washington	1195	15
11.	Rock Creek, Klickitat County, Washington	760	10
12.	Wallula Gap, Walla Walla County, Washington	1190	13
13.	Powatka, Wallowa County, Oregon	1470	19
14.	Grande Ronde, Asotin County, Washington	1460	32
15.	Snake River Bend, Asotin County, Washington	2080	25
16.	Keuterville-Salmon River, Idaho County, Idaho	1920	17
17.	Lawyers Canyon, Clearwater County, Idaho	1825	18
18.	Tygh Ridge, Wasco County, Oregon	610	8
19.	Beef Hollow, Gilliam County, Oregon	1555	22
20.	Sixmile, Gilliam County, Oregon	480	7
21.	Minam, Union County, Oregon	1077	20
22.	Joseph Creek, Wallowa County, Oregon	2010	23
23.	Imnaha, Wallowa County, Oregon	2465	31
24.	Cow Canyon, Wasco County, Oregon	750	11
25.	Picture Gorge, Grant County, Oregon	720	14
26.	Crooked River, Crook County, Oregon	830	11
27.	Mauzy Mountains, Crook County, Oregon	410	5
28.	Pine Creek, Baker County, Oregon	1225	12

Salmon Rivers in the southeastern part of the plateau. A preliminary petrographic investigation of each flow in the 28 sections has been made, and a few chemical analyses of the rocks are herewith reported (tables 2, 3, 4, and 5). Geologic relations to contiguous formations are based on the mapping of 5 fifteen-minute quadrangles, and of all or part of 9 thirty-minute quadrangles, supplemented by considerable reconnaissance of other parts of the lava field. Only a few of the major results are given here; the purpose of this paper is to give a general, if still incomplete, picture of the regional variations in composition and stratigraphic position of the lavas within this huge area of flood basalts.

FISSURE ERUPTIONS AND DIKE SWARMS

The basalt flows emerged as fissure eruptions (Russell, 1901, p. 29; Merriam, 1901, p. 304; Lindgren, 1901, p. 741; Fuller, 1927, p. 228; Waters, 1950, p. 1533). The feeders are grouped in huge dike swarms concentrated within the limits of definite areas. In figure 1 the location of those dike swarms whose connection with the Columbia River basalt has been established are indicated by capital letters G, C, M, and T. None of these swarms have been thoroughly mapped or studied, and the following notes regarding them are based on reconnaissance.

G. Grande Ronde dike swarm.—This huge dike swarm, located near the northeast corner of the State of Oregon, is represented by scores of dikes, 10 to 70 feet thick, many of which can be traced for miles. They are magnificently exposed on the steep walls of the Grande Ronde River and its tributaries between Troy and Shoemaker Creek (pl. 2-B), and in the lower part of the canyon of Joseph Creek. Farther east dikes continue to appear, but in diminishing numbers, in the canyon of Snake River and at least as far east as Grave Creek near Keuterville, Idaho. Thus the dike swarm is at least 45 miles long and 10 to 20 miles wide.

Although individual dikes may curve or be irregular in detail, most have trends within the range north-south to north 30° east. A definite connection between a dike in this swarm and a flow of the Columbia River basalt has been reported and illustrated by Fuller (1927), and the writer has found additional examples. From the nature of fissure eruption, however, such unbroken connections must be extremely rare because a slight amount of withdrawal of the magma into the feeding fissure, or a resurgence of lava up the fissure after the flow has solidified will break the connection. Indirect but conclusive evidence of a genetic connection between dikes and adjacent flows has been seen at several localities. Criteria observed include an abrupt change from upright to inclined columnar jointing within the flow immediately adjacent to a dike, the cupping down of the top of some flows into a moatlike depression along the course of a dike, and the formation on the top of other flows of a raised edge or "levee" composed of thin gushes of lava and fragments of splattery clinker. In Shoemaker Canyon the direct connection of the chilled selvage of one dike with the chilled base of an adjacent flow was also observed, although the interior of this dike cuts upward through the flow with a sharp boundary. Many dikes are multiple (pl. 2-B) and fed more than one flow (Waters, 1950).

C. Cornucopia dike swarm.—The great swarm of dikes exposed in the eastern part of the Wallowa Mountains about 70 miles south of the Grande Ronde swarm was first described by Lindgren (1901, p. 593, 741-742). "At no place," he wrote, "are they exposed on such a magnificent scale as in the Bonanza Basin, near Cornucopia" and he also pointed out the relation of these dikes to the surrounding flows of Columbia River basalt. The dikes trend predominantly north-south. Goodspeed (1959, p. 213-229) has recently published some interesting petrographic details regarding some of the dikes in this swarm and has outlined the wide extent of the dikes to the north and northwest from Cornucopia. Stearns (1950, p. 55) reports a great swarm of dikes extending from Halfway (9 miles southeast of Cornucopia) to the Seven Devils region in Idaho. It appears, therefore, that the Cornucopia swarm may be fully as extensive and voluminous as the Grande Ronde swarm.

M. Monument dike swarm.—In his pioneer publication on the John Day basin Merriam (1901, p. 304) mentioned the occurrence of a group of basalt dikes which he considered to be feeders of the Columbia lava. This dike swarm is best exposed, and apparently the dikes are most numerous, in the canyon of the North Fork of John Day River between Monument and Kimberly. Near Monument sills and irregular cross-cutting masses of diabase also invade the John Day and Clarno formations. Thayer (1957) has traced the dike swarm between the Aldrich Mountains and the Monument-Kimberly area—a distance of about 40 miles—and has mapped the parts of the swarm that lie in the Mount Vernon and Aldrich Mountains quadrangles (Thayer, 1956a, b). Ray E. Wilcox is mapping the area near Monument. Most of the dikes in this swarm trend about north 30° west.

T. Tieton dike swarm.—Closely spaced dikes that trend north-south invade Oligocene and Miocene sedimentary and volcanic rocks along Tieton River from Rimrock to within about 5 miles of the junction of the Tieton with Naches River. From here they extend northward, and though not well exposed in the intervening area, probably connect with the group of dikes and irregular diabase intrusions about 25 miles to the north (headwaters of Manastash Creek) that Smith and Calkins mapped as feeders of the Yakima basalt (Smith, 1904, p. 8; Smith and Calkins, 1906, p. 7). Chappell (1936, p. 384) suggested that the huge Teanaway dike swarm, which lies still farther north in the Wenatchee Mountains, may contain feeders of the Columbia River basalt in addition to feeders of the Eocene Teanaway lavas (Smith, 1904; Smith and Calkins, 1906). Numerous dikes are found south of the Tieton, as well, but their southernmost limit is not known.

The Tieton dike swarm is much more complex than the ones previously described. This swarm, like numerous other belts of near-surface intrusions clustered along north-south zones within the Cascade Range, contains a wide assortment of igneous rocks of various ages and compositions. In addition to feeders of the Yakima basalt, this swarm includes great numbers of porphyritic olivine andesite dikes and olivine basalt dikes—perhaps feeders of the olivine-hypersthene andesites and basalts of the Fives Peak formation that underlie the Yakima basalt of the Tieton area. Dikes and irregular masses of

diorite porphyry, dacite, and rhyolite are also minor components of this dike swarm.

Lower Columbia River and Astoria regions.—The writer has not worked on the Miocene basalts of the Lower Columbia Valley west of the Cascade Mountains. Dike feeders of these basalts have been reported in the Saint Helens quadrangle northwest of Portland (Wilkinson, Lowry, and Baldwin, 1946), and great numbers of basalt dikes can be seen across Columbia River between Woodland and Castle Rock, Washington. Some of the latter may be feeders of the Goble volcanic series of Eocene age. Dikes and sills genetically connected with the Columbia River basalt have been reported near Astoria (Warren, Norbistrath, and Grivetti, 1945) and in the upper part of the Nehalem River basin (Warren and Norbistrath, 1946, p. 233).

Returning to a consideration of the Columbia River basalt plateau as a whole, perhaps the most notable thing is the complete absence of feeders over great areas. Most parts of the huge lava field show no dikes. Even isolated dikes are not found far from the borders of the great swarms, and they could scarcely be overlooked among the excellent canyon exposures that prevail over wide areas of the plateau. To be sure other dike swarms may be hidden beneath a cover of soil or sedimentary rock, especially in the poorly exposed central part of the plateau. Moreover the topmost flows of flood basalt may hide dike swarms that contributed to lower flows in the lava sequence. It is interesting, however, that all the known dike swarms are concentrated near the southern and western margins of the great lava field (pl. 1). If the bulk of the lavas came only from these dikes, many flows must have traveled over 100 miles from their source. Evidence on the direction of movement of individual flows in the northern part of the lava field consistently indicates advance toward the highlands, which formed a shoreline for the encroaching sea of basalt on the north and east. (For criteria used in determining the direction of flow see Waters, 1960).

No shield volcanoes or cinder cones have been found, although both are common among the Pliocene-Quaternary olivine basalts that overlie the Columbia River basalt.

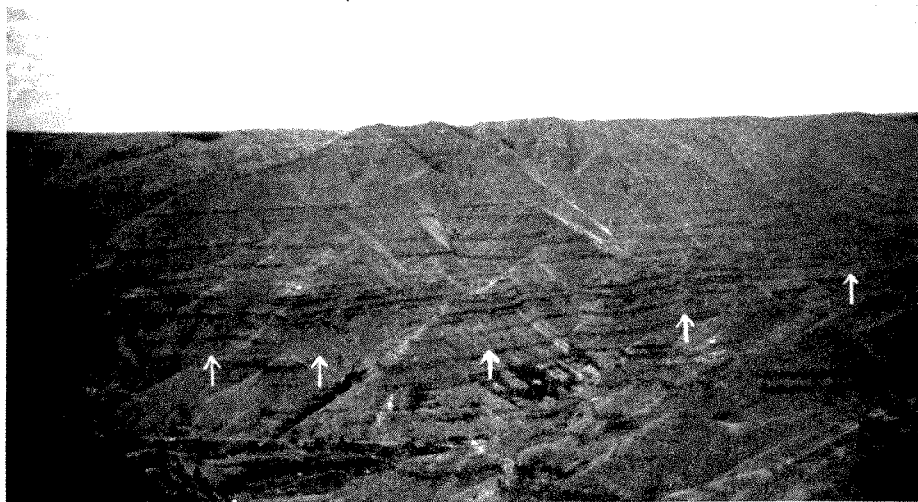
TWOFOLD DIVISION OF THE COLUMBIA RIVER BASALT

Remarkably homogeneous lava showing little variation in chemical and mineral composition except in relative amounts of glass (see tables 3 and 7) covers at least two-thirds of the area underlain by the Columbia River basalt floods. This is the Yakima basalt of Smith (1901, p. 15). Its monotony in composition is broken only by a late more basic variant that was erupted chiefly during the waning stages of vulcanicity after folding and faulting had started to deform the lava field in early Pliocene time. Typical Yakima basalt forms the characteristic flows described by Russell from Douglas County, the flows that banked against the plutonic and metamorphic highlands of northeastern Washington and western Idaho, the lavas at the surface of the plateaus of eastern Washington and northeastern Oregon, and all but the lower flows of the Grangeville plateau in Idaho.

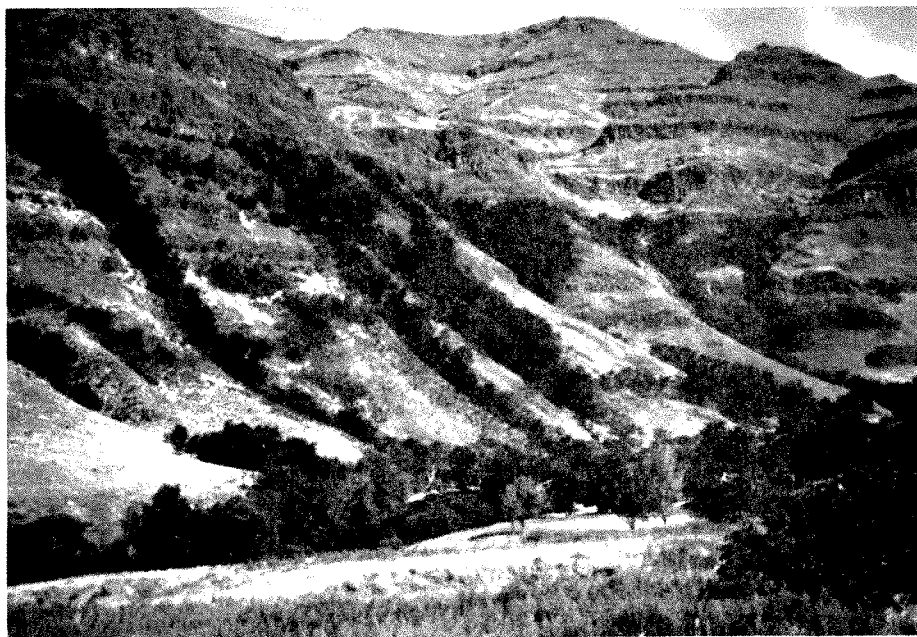
But along the southern margin of the lava field the widespread and homogeneous Yakima basalt rests unconformably upon a more diversified and

PLATE 1

Unconformity within the Columbia River basalt

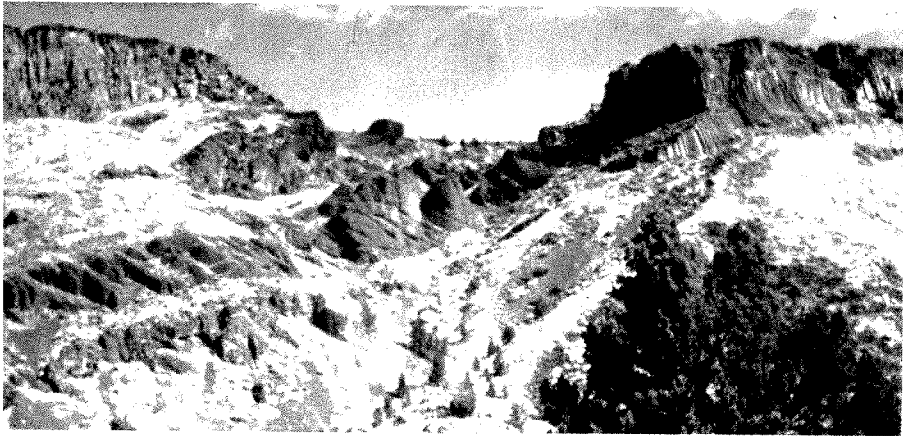


A. Slightly tilted and eroded flows of Picture Gorge basalt are overlapped toward the right by successively higher, nearly horizontal flows of Yakima basalt. The surface of unconformity is indicated by the arrow points. East wall of Imnaha River canyon at Grizzly Ridge. View shows a 3400-foot vertical section of basalt flows; lateral extent of view about 7 miles.



B. The upper limit of vegetation marks the emergence of springs at the unconformity between overlying permeable Yakima basalt and underlying nearly impermeable Picture Gorge basalt. Note the cluffed character of the Yakima flows and the more rounded slopes characteristic of the Picture Gorge flows. West wall of Imnaha River canyon one mile downstream from Imnaha, Oregon.

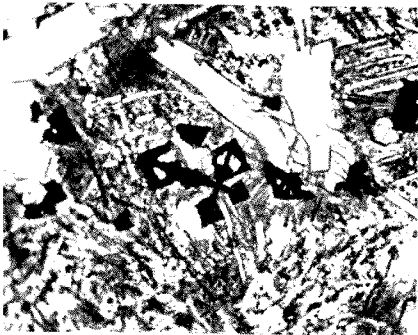
PLATE 2



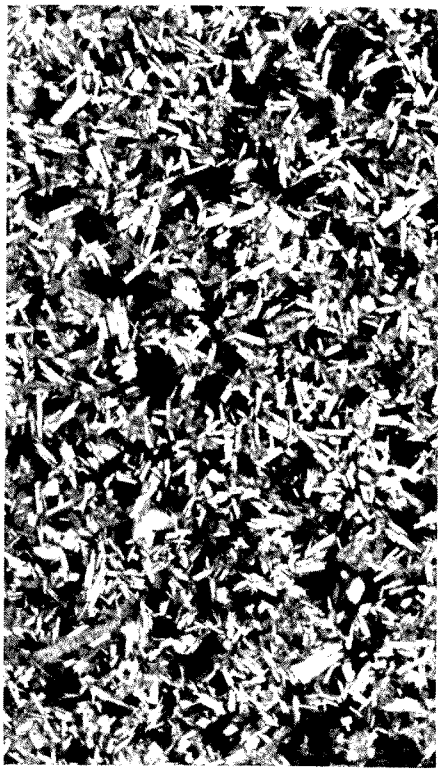
A



B



D



C

Structural and textural features of the
Columbia River basalt.

somewhat older sequence of basalts (tables 2 and 6). This twofold division of the Columbia River basalt is subtle and easily overlooked in the field: in some places it can be picked up only after the observer becomes sensitive to rather elusive differences in physical appearance of the flows which reflect minor differences in mineralogy.

The division of the Columbia River basalt into two distinct formations is especially clear on the walls of the mile-deep canyons of the Salmon, Snake, and Imnaha Rivers of northeastern Oregon and adjacent Idaho. Here the junction between the two basalts is easily located by an unconformity between them (pl. 1), by the presence along the contact of local patches of coarse volcanic conglomerate containing fragments of the underlying basalt, and by the more impermeable character of the lower basalt, which, in places, causes a conspicuous line of springs and heavy vegetation along the contact (pl. 1-B).

Farther west, in the Ochoco Mountains and John Day basin, the older basalts are not confined to the deeper parts of canyons: they come to the surface over wide areas from which the younger basalts are generally absent. In the John Day basin the older basalt sequence makes up the sections at Picture Gorge and Turtle Cove that Merriam redefined as the "Columbia lava." But a few miles to the northwest it disappears unconformably beneath the homogeneous Yakima basalt.

Further discussion of structural and stratigraphic relations is deferred until the chemical and mineralogical differences between these two distinct sequences of lavas are outlined. In the following discussion the southern and older lavas will be called the Picture Gorge basalt, and the northern and younger the Yakima basalt. Near the end of this paper, proposals are made to formalize these terms as formation names and to elevate Columbia River basalt to the status of a stratigraphic group.

CHEMICAL AND MINERALOGICAL DIFFERENCES BETWEEN THE PICTURE GORGE AND YAKIMA BASALTS

The two divisions of the Columbia River basalt recognized on stratigraphic grounds also show characteristic differences in chemical and mineralogical composition. Table 2 lists available analyses of the older, or Picture Gorge basalt. Table 3 presents analyses of the Yakima basalt exclusive of its more basic late variant, a few analyses of which are listed in table 4. Table 5 gives the "average" analysis of each of the three chemically distinctive types of Columbia River basalt, along with averages of the Pliocene-Quaternary olivine basalts of the Cascade Mountains, the basalts from the Snake River Plain, and various "average" basalts from other parts of the world.

A. Unconformity between tilted Columbia River basalt (center) and horizontal Pliocene-Quaternary olivine basalt (cliffed palisades on skyline). Crooked River canyon, 18 miles upstream from Prineville, Oregon.

B. Multiple basalt dike cutting Yakima basalt flows. Grande Ronde River near Shoemaker Canyon, Washington.

C. Unusual textural variant characteristic of the Late Yakima flows in the Cascade foothills. Note tangled coarse microlites of plagioclase enclosing large patches of partly crystallized glass (dark spots). $\times 50$.

D. Skeleton crystals of a titaniferous opaque in Late Yakima basalt. $\times 140$.

TABLE 2
Chemical analyses, Picture Gorge type, Columbia River basalt

	1	2	3	4	5	6	7	8	A	B
SiO ₂	50.02	49.77	49.5	49.4	48.34	47.7	47.4	49.94	49.3	49.5
Al ₂ O ₃	15.43	15.64	14.6	14.5	15.85	17.0	16.0	15.29	15.6	15.5
Fe ₂ O ₃	4.20	3.00	2.5	3.1	2.75	3.5	3.3	4.23	3.5	3.8
FeO	8.31	8.19	9.4	8.3	8.54	7.4	8.5	7.82	7.8	7.8
MgO	6.01	6.32	7.1	7.1	6.74	6.5	7.6	5.73	6.5	6.2
CaO	9.93	9.77	10.8	10.4	10.46	11.2	10.0	9.91	10.3	10.2
Na ₂ O	2.38	3.11	2.9	2.8	2.88	2.6	2.6	3.04	2.7	2.8
K ₂ O	0.50	0.71	0.45	0.52	0.53	0.36	0.40	0.64	0.5	0.6
H ₂ O ⁺	1.02	0.62			0.73			0.36		
H ₂ O ⁻	0.48	0.93	1.0	1.9	0.88	2.2	2.4	0.98	1.8	1.6
TiO ₂	1.16	1.43	1.5	1.5	1.65	1.6	1.7	1.69	1.6	1.6
P ₂ O ₅	0.26	0.24	0.27	0.26	0.29	0.34	0.32	0.26	0.3	0.3
MnO	0.24	0.19	0.22	0.20	0.19	0.18	0.19	0.20	0.2	0.2
CO ₂		0.01	0.08	0.05	0.02	0.05	0.04		0.04	
Sum	99.94	99.93	100.32	100.03	99.84	100.63	100.45	100.09		

- Twelfth flow from top, Picture Gorge section (no. 26), Grant County, Oregon. Herdman, analyst. (New analysis).
- Fourteenth flow from base, Spray quadrangle, Wheeler County, Oregon. P. M. Montalto, analyst, USGS serial no. F-2536. (New analysis, courtesy D. H. Lindsley)
- Little Horse Spring, Post quadrangle, Crook County, Oregon. P. L. D. Elmore and K. E. White, analysts, USGS lab. no. 142176. (New analysis)
- One mile east of Drakes Butte, Maury Mountains, Crook County, Oregon. P. L. D. Elmore and K. E. White, analysts, USGS lab. no. 142177. (New analysis)
- Second flow from base, Spray quadrangle, Wheeler County, Oregon. P. M. Montalto, analyst, USGS serial no. F-2535 (New analysis, courtesy D. H. Lindsley)
- Third flow from base, Spray quadrangle, Wheeler County, Oregon. (New analysis, courtesy D. H. Lindsley)
- Sixth flow from base, Spray quadrangle, Wheeler County, Oregon. (New analysis, courtesy D. H. Lindsley)
- Composite analysis of weighed samples from each of 14 flows, Picture Gorge section (no. 26), Grant County, Oregon. B. Smith and R. B. Ellestad, analysts, Grout lab. no. R-966. (New analysis)
- Average of 16 analyses. Includes the analyses of Columns 1 to 7, plus the following nine unpublished analyses:
 - Picture Gorge, Grant County, Oregon, USGS Lab. no. 51-1715CW (T. P. Thayer)
 - Picture Gorge, Grant County, Oregon, USGS Lab. no. 51-1717CW (T. P. Thayer)
 - Picture Gorge, Grant County, Oregon, USGS Lab. no. 51-1718CW (T. P. Thayer)
 - 1½ mi NE Mt. Vernon, Oregon, USGS Lab. no. 1D-18385DCD (T. P. Thayer)
 - Johnnycake Mt., Grant County, Oregon, USGS Lab. no. D-1779 (R. E. Wilcox)
 - Johnnycake Mt., Grant County, Oregon, USGS Lab. no. D-1780 (R. E. Wilcox)
 - Johnnycake Mt., Grant County, Oregon, USGS Lab. no. D-1781 (R. E. Wilcox)
 - Riggins Quad, Idaho County, Idaho, USGS Lab. no. 148441 (W. B. Hamilton)
 - Riggins Quad, Idaho County, Idaho, USGS Lab. no. 148444 (W. B. Hamilton)
- Average of two times Column A plus Column 8

As shown in these tables, and also in the standard variation diagram (fig. 2), there are significant chemical differences between the older Picture Gorge basalt and the Yakima basalt. The older lavas are higher in Al₂O₃, MgO, and CaO, and lower in SiO₂, K₂O, and TiO₂. Moreover there appear to be no transitional varieties; the analyzed specimens fall distinctly into one group or another, and this is also true of the large number of modes measured from thin sections of these rocks.

TABLE 3
Chemical analyses, Yakima type, Columbia River basalt

	1	2	3	4	5	6	7	8	A	B
SiO ₂	54.60	54.50	53.72	53.54	53.1	53.13	54.66	53.71	53.9	53.8
Al ₂ O ₃	13.52	14.43	13.64	14.10	13.8	14.06	13.78	13.88	13.8	13.9
Fe ₂ O ₃	1.96	2.17	2.46	1.73	3.2	2.25	2.12	3.65	2.3	2.6
FeO	10.46	8.80	9.96	10.33	9.4	9.45	9.30	8.27	9.8	9.2
MgO	3.52	4.24	4.63	4.59	4.2	4.72	3.69	3.93	4.2	4.1
CaO	7.45	8.01	8.27	8.54	7.7	8.39	7.44	7.59	8.0	7.9
Na ₂ O	3.09	3.05	2.94	3.14	2.9	2.84	3.05	3.05	3.0	3.0
K ₂ O	1.74	1.29	1.24	1.21	1.5	1.24	1.67	1.65	1.4	1.5
H ₂ O ⁺	0.87	1.09	1.05	0.26		0.79	0.99	0.69		
H ₂ O ⁻	0.10	0.29	0.40	0.03	1.6	0.54	0.29	0.53	1.1	1.2
TiO ₂	2.54	1.69	1.44	2.01	2.2	1.84	2.19	2.17	2.0	2.0
P ₂ O ₅	0.09	0.21	0.31	0.35	0.44	0.33	0.36	0.47	0.3	0.4
MnO	0.18	0.10	0.21	0.22	0.20	0.19	0.18	0.20	0.2	0.2
CO ₂	None	tr	None		0.05				tr	
Sum	100.07	99.87	100.27	100.05	100.29	99.77	99.72	99.79		

1. Hackly basal flow, 5 mi west of Waterville, Douglas County, Washington. Herdsman, analyst. (new analysis)
 2. Cleadum Ridge, 4 mi southwest of Cle Elum, Kittitas County, Washington. Geo. Steiger, analyst. (Smith, 1903a, p. 8)
 3. Eighth flow from top, Crescent Bar (No. 2) section, Grant County, Washington. Herdsman, analyst. (new analysis)
 4. East of Oregon State Training School, near Salem, Oregon. A. Willman, analyst. (Thayer, 1937, p. 1622)
 5. Five miles north of New Meadows, Riggins quadrangle, Adams County, Idaho. P. L. D. Elmore, S. D. Botts, and K. E. White, analysts, USGS Lab. no. 15190 (new analysis, courtesy, W. B. Hamilton)
 6. Composite analysis of weighed samples from each of 9 flows, Crescent Bar section (no. 2), Grant County, Washington. B. Smith and R. B. Ellestad, analysts, Grout Lab. no. R-964. (new analysis)
 7. Composite analysis of weighed samples from each of 19 flows, Lawyers Canyon Section (no. 17), Lewis County, Idaho. B. Smith and R. B. Ellestad, analysts, Grout Lab. no. R-964. (new analysis)
 8. Composite analysis of weighed samples from each of 32 flows, Grande Ronde section (No. 14), Asotin County, Washington. B. Smith and R. B. Ellestad, analysts, Grout Lab. no. R-965. (new analysis)
- A. Average of columns 1 to 5.
B. Average of columns A + 6 + 7 + 8.

The chemical differences are clearly reflected in the mineralogy. Table 6 gives the modes of 14 flows of the older basalt exposed in the continuous section (number 25) at Picture Gorge, and of 13 flows that lie unconformably beneath the Yakima basalt in the thick section (number 23) on the west wall of the Imnaha River canyon near Imnaha, Oregon. Table 7 lists the same kind of data for two sections of the Yakima basalt, the first (number 2) at Crescent Bar in the northwestern part of the plateau, the other (number 14) a section comprising 32 flows on the north wall of the Grande Ronde Canyon in the southeastern corner of Washington. The Grande Ronde section lies within one of the areas of feeder dikes; the Crescent Bar section is far removed from any known dike swarm.

TABLE 4

Chemical analyses, Late Yakima and Ellensburg flows, Columbia River basalt

	1	2	3	4	A
SiO ₂	49.08	50.0	49.6	51.44	50.0
Al ₂ O ₃	13.71	14.1	12.8	13.29	13.5
Fe ₂ O ₃	1.25	2.1	1.9	2.16	1.9
FeO	13.02	11.6	13.2	12.00	12.5
MgO	4.58	4.3	4.4	4.28	4.4
CaO	8.44	8.1	8.4	8.28	8.3
Na ₂ O	3.17	2.8	2.5	2.93	2.9
K ₂ O	1.31	1.4	1.3	1.40	1.4
H ₂ O ⁺	0.90		1.0	0.66	0.9
H ₂ O ⁻	0.20	1.8		0.07	
TiO ₂	3.56	3.2	3.4	2.80	3.2
P ₂ O ₅	0.73	0.79	0.81	0.61	0.7
MnO	0.25	0.24	0.27	0.23	0.25
CO ₂		<0.05	0.31		0.09
Sum	100.20	100.48	99.89	100.15	

1. The Dalles, Oregon, H. S. Washington, analyst (Washington, 1922, p. 779)
 2. Turtle Lake quadrangle, Washington, Specimen no. 6B-501. P. L. D. Elmore, S. D. Botts, and M. D. Mack, analysts (Becraft and Weis, in press)
 3. Turtle Lake quadrangle, Washington, Specimen no. 7B-261. P. L. D. Elmore, S. D. Botts, and M. D. Mack, analysts (Becraft and Weis, in press)
 4. 4 miles west of Stayton, Oregon. (Thayer, 1937, p. 1622)
- A. Average of columns 1 to 4

Most flows of Picture Gorge basalt are nearly holocrystalline, although some are exceedingly fine grained. Even the coarsely crystalline ones generally contain at least a little pale brown glass. The Yakima flows are rich in dark-colored tachylite: most contain 20 percent or more, and many over 40 percent. The modes of all rocks listed in the tables were measured on specimens taken from the lower tier of columns, well above the basal chill zone, and so contain less glass than the flows as a whole. Nearly all flows of Yakima basalt are non-porphyrific or else have only tiny microphenocrysts. On the other hand about one-fourth of the Picture Gorge flows contain phenocrysts of plagioclase, pyroxene, and olivine.

Detailed studies of the minerals in the Columbia River basalt are under way but not yet complete; only a few of the main features are summarized here. Pyroxene, plagioclase, and olivine show some systematic differences in the two kinds of basalt. Most flows of Yakima type contain plagioclase close to An₅₀, that in the Picture Gorge type is more calcic and shows more zoning. All pyroxenes are monoclinic and are optically positive. Most Yakima flows contain a clear to pale honey-colored pyroxene with a 2V of about 40 to 45 degrees. In many rocks it is zoned to a deeper honey-golden pyroxene. Pyroxene in rocks of the Picture Gorge type is more variable: pale golden-brown pyroxene with a 2V around 50 to 52 degrees is common, but in the coarser-

TABLE 5
Average chemical composition of Columbia River basalts, and other basalts

	Columbia River Basalts					Nockolds (1954) World Averages			
	Picture Gorge basalt	Yakima basalt	Late Yakima and Early Ellensburg flows	Olivine basalts from central part of Cascade Range	Olivine basalts from Snake River Plain (compilation by H. Powers, 1960)	Normal tholeiitic basalt	Tholeiitic olivine basalt	Tholeiitic andesite	"Central" basalt
SiO ₂	49.3	53.8	50.0	49.79	46.11	50.83	47.90	51.43	51.33
Al ₂ O ₃	15.6	13.9	13.5	16.74	14.54	14.07	11.84	13.05	18.04
Fe ₂ O ₃	3.5	2.6	1.9	2.65	2.70	2.88	2.32	3.36	3.40
FeO	7.8	9.3	12.5	7.82	10.15	9.00	9.80	9.74	5.70
MgO	6.5	4.1	4.4	7.16	7.48	6.34	14.07	5.28	6.01
CaO	10.3	7.9	8.3	9.07	9.73	10.42	9.29	8.78	10.07
Na ₂ O	2.7	3.0	2.9	3.32	2.41	2.23	1.66	3.18	2.76
K ₂ O	0.5	1.5	1.4	0.82	0.61	0.82	0.54	1.04	0.82
H ₂ O ⁺	} 1.8	1.2	0.9	0.41	0.46	0.91	0.59	0.87	0.45
H ₂ O ⁻					0.58				
TiO ₂	1.6	2.0	3.2	1.71	2.93	2.03	1.65	2.60	1.10
P ₂ O ₅	0.3	0.4	0.7	0.31	0.67	0.23	0.19	0.48	0.16
MnO	0.2	0.2	0.25	0.17	0.20	0.18	0.15	0.19	0.16
CO ₂	0.04		0.09	0.02	0.04				
Number of analyses	16	8	4	13	38	137	28	26	56

grained rocks it may be zoned to, or proxied for, by a pale purplish brown titanpyroxene of small (about 45°) 2V.

Analcime is a common accessory in the older basalts but is vanishing rare in Yakima flows. Cavity fillings of opal are common in the Yakima basalt, especially from areas near dike swarms, or where lava poured into water and formed pillow lava - palagonite complexes.

The Picture Gorge flows are characterized by a small (about 5 percent) but uniform content of iron-rich olivine, which in most rocks is wholly or partly altered to saponite. Except for its late basic variant, the Yakima basalt shows only traces of olivine, or at most less than 2 percent. The Picture Gorge basalt also contains more chlorophaeite and its characteristic decomposition products than does the Yakima basalt. Chlorophaeite, first described from the Columbia River plateau by Peacock and Fuller (1928), is an apple-green iron-rich mineraloid, completely isotropic to light and X-rays when fresh. It is unstable, however, and freshly broken surfaces alter within a few months to a sooty black material, or after long-continued weathering to waxy dark brown

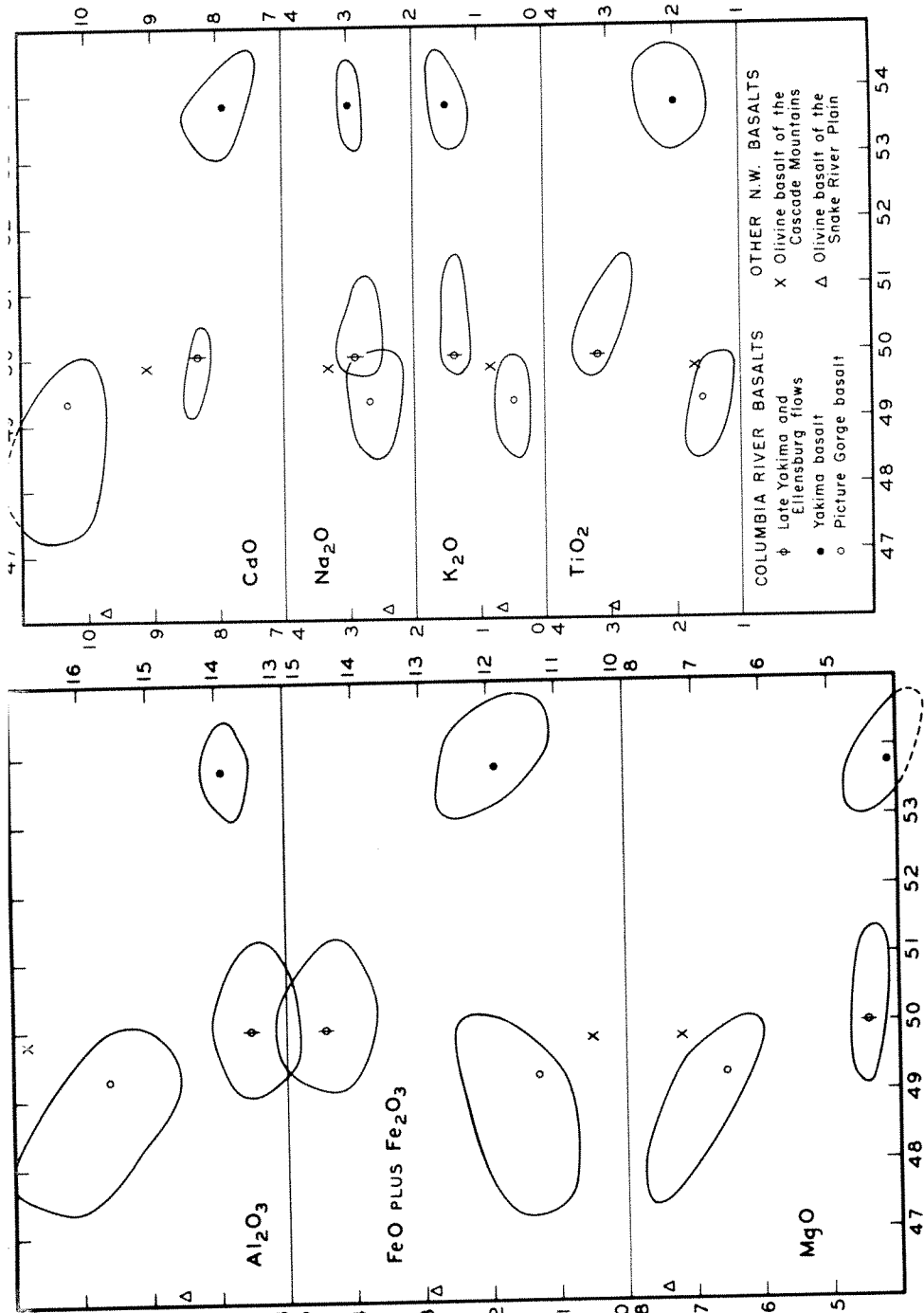


Fig. 2. Variation diagram, basaltic rocks of the Pacific Northwest. Symbols indicate average composition of: (a) the three chemical variants of the Columbia River basalt, (b) the olivine basalt of the Cascade Mountains, and (c) the olivine basalt of the Snake River plain (from table 5). Spaces enclosed by lines show areas within which available chemical analyses of the three variants of the Columbia River basalt fall.

TABLE 6

Modes, Picture Gorge basalt: no. 25, Picture Gorge section; no. 23, lower part of Imnaha section

(Top) No. 25 Picture Gorge	Plagioclase	Monoclinic Pyroxene	Olivine (including saponite)	Glass	Chlorophaeite (including decomposition products)	Opaque	Zeolites
25-1	43.6	42.2	2.6	1.8	1.2	7.6	1.0
25-2	40.0	37.0	6.2	6.2	4.8	3.6	2.2
25-3	40.4	30.2	7.6	3.8	13.6	3.8	0.6
25-4	41.4	33.6	5.4	6.0	7.8	5.0	0.8
25-5	39.6	42.0	2.8	1.4	6.2	7.6	0.4
25-6	37.2	37.0	6.8	4.2	8.0	6.0	0.8
25-7	33.2	39.2	2.2	10.4	4.0	10.8	0.2
25-8	36.8	37.0	2.4	20.2	0.2	3.4	none
25-9	42.8	37.0	6.2	4.4	3.4	6.0	0.2
25-10	37.8	36.4	8.2	3.8	7.8	6.0	none
25-11	39.0	34.6	4.2	13.8	2.0	6.4	none
25-12	39.0	42.0	1.6	4.6	3.6	8.6	0.6
25-13	40.6	36.4	7.4	2.8	6.2	6.2	0.4
25-14	39.2	40.2	2.4	4.6	5.4	7.4	0.8
Average	39.2	37.5	4.7	6.3	5.3	6.3	0.6
No. 23							
Imnaha							
23-20	41.0	33.6	4.4	10.8	3.0	7.2	none
23-21	46.5	30.5	2.7	7.0	7.3	6.1	trace
23-22	46.4	32.9	2.1	5.0	5.1	7.6	0.9
23-23	54.2	27.6	2.2	7.4	0.4	7.4	0.8
23-25	44.0	37.7	6.3	1.8	1.7	8.5	trace
23-26	56.4	25.4	12.6	1.0	0.2	2.8	1.6
23-27	54.4	20.0	13.0	2.0	1.2	6.4	3.0
23-28	49.2	31.2	4.0	4.0	0.4	10.8	0.4
23-29	34.2	29.2	6.6	19.2	1.8	9.0	trace
23-30	39.2	25.0	7.4	13.2	6.6	8.2	0.4
23-31	45.6	31.8	11.4	5.6	0.8	4.8	none
Average	46.5	29.5	6.7	7.0	2.6	7.2	0.7

or reddish brown substances. In about half of the flows it is decomposed, even in the fresh rocks from deep excavations; in some of these it is fresh in the chilled base of the flow but decomposed in the flow interiors and along the margins of vesicles where volatiles could break it down during the last stages in the cooling history of the flow. X-rays show that the decomposition products are chiefly iron oxides and clay minerals, among which nontronite, saponite, montmorillonite, and celadonite appear to be most common. Peacock held that chlorophaeite replaces olivine, but his work was done before X-ray identifications became routine, and it seems almost certain that he confused the abundant deep greenish iron-rich saponite, which pseudomorphs ferriiferous olivine in many Picture Gorge basalts, with chlorophaeite. The writer's observations

TABLE 7

Modes: Yakima basalt: No. 2, Crescent Bar section; No. 14, Grande Ronde section

No. 2 Crescent Bar (Top)	Plagio- clase	Mono- clinic pyroxene	Olivine (including saponite)	Glass	Chlorophaeite (including decomposition products)	Opagues
2-2	36.2	29.1	1.4	22.2	4.8	6.3
2-4	30.5	25.9	none	30.6	5.7	7.3
2-51	30.9	28.6	trace	28.6	2.9	9.0
2-52	28.5	29.0	0.7	29.9	2.6	9.2
2-8	30.4	25.9	none	35.5	1.8	6.5
2-10	29.8	31.0	0.4	29.2	0.6	8.9
2-11	30.4	26.4	none	32.8	0.4	10.0
Average	31.0	28.0	0.03	29.8	2.7	8.2
No. 14 Grande Ronde						
14-1	27.8	41.0	none	19.5	3.5	8.2
14-2	23.7	37.2	trace	29.6	1.1	8.5
14-2a	26.8	20.8	2.2	32.4	5.9	11.9
14-4	18.2	23.0	1.8	41.8	6.8	8.2
14-6	30.0	24.1	1.7	28.2	5.1	10.8
14-8	37.8	39.3	1.7	12.0	5.5	3.6
14-8a	24.3	44.5	0.4	16.0	6.9	7.9
14-9	27.2	28.8	none	30.3	3.1	10.5
14-10	33.3	35.0	none	23.5	none	8.1
14-11	30.8	29.6	none	24.7	2.7	12.2
14-12	33.0	31.1	0.4	18.2	3.8	13.5
14-13	31.1	34.4	none	23.8	none	10.7
14-14	35.2	30.2	none	21.8	4.5	8.3
14-15	24.2	32.8	2.1	27.6	3.7	9.5
14-16d	16.0	37.2	0.2	32.6	1.4	12.6
14-17	13.6	30.3	none	43.5	1.8	10.8
14-18	33.2	21.0	1.0	31.9	5.9	7.1
14-19	25.0	35.2	trace	27.0	none	12.7
14-20	32.0	30.2	0.6	23.6	7.5	6.1
14-21	36.5	25.9	0.6	25.4	5.4	6.6
14-22	28.5	29.6	1.4	24.0	5.6	10.8
14-23	44.2	34.2	1.6	10.2	3.0	6.8
14-24	46.8	36.2	0.4	9.8	none	6.8
14-25	36.8	33.2	1.8	17.6	3.0	7.6
14-26	40.4	33.6	0.6	16.4	4.4	4.6
14-27	33.8	47.4	1.6	10.4	2.2	3.6
14-28	39.0	33.6	0.6	19.0	4.4	4.2
14-29	41.2	37.0	0.6	10.8	1.8	8.6
14-30	39.4	37.2	none	14.0	1.2	8.2
14-31	42.2	39.4	0.2	14.4	none	3.8
14-32	32.4	52.6	none	9.4	none	5.6
14-33	45.0	37.6	0.4	10.8	none	6.2
Average	32.1	33.9	0.7	21.9	3.1	8.3

are that chlorophaeite is invariably interstitial, or else is confined to oval segregations within basalt glass. Its decomposition products may wander widely, however, producing stains on feldspars and ferromagnesians. Flows containing abundant chlorophaeite weather to a deep orange brown; flows without it generally weather to neutral gray or greenish gray shades.

The richness of the Picture Gorge flows in olivine and in chlorophaeite is responsible for one of the most useful criteria to distinguish them from the Yakima basalt in the field: most of the olivine and chlorophaeite-rich flows have undergone a slight deuteric alteration that gives the lava a dark color and a characteristic greasy or waxy appearance. On weathering this greasy type of lava swells and develops innumerable small cracks much like the craze on the surface of some kinds of pottery. Continued swelling and opening of the cracks causes the lava to disintegrate into a coarse grus of small angular fragments. The decomposition and disintegration of the rock is more intense in the interiors of joint columns than along their edges, and is more prevalent in the centers of flows than in their chilled tops and bottoms. The immediate cause of the crazing and swelling of the rock is its content of clay minerals derived mainly from the breakdown of olivine and chlorophaeite. The disintegration of the coarsely columnar interiors of the flows by these alterations causes the Picture Gorge basalts to weather into generally rounded slopes with softened and blurred profiles in contrast to the bold cliffs of "rimrock" carved from the resistant lower tier of columns in the flows of Yakima basalt.

In the older, greasy-appearing basalts that occupy the lower part of the Imnaha Canyon (pl. 1-B) such alterations significantly affect the joint pattern. Columnar joints in the lower parts of the flows are swelled shut, and alteration of the flow centers has produced a massive tightly jointed rock that is practically impermeable to water. Therefore many springs emerge on the walls of the Imnaha Canyon at the unconformity between the overlying well-jointed Yakima basalt and the Picture Gorge basalt.

In general the Yakima basalt is nearly free of these alterations. Near dike feeders some flows show blotchy streaks where collapsed vesicles contain a little chlorophaeite and have retained enough volatile material to produce a slight amount of montmorillonitic alteration of the vesicle walls. Some of these blotchy flows also contain opal in cavities, and a few show small ball-like clusters or pseudocubic aggregates of cristobakite. Opal was disregarded in making the modes shown in table 7, but it is unquestionably responsible for the higher silica content shown in the chemical analysis of the rocks from Waterville (column 1, table 3) and from Clealum ridge (column 2, table 3). Each of these flows contains about 1 percent of hyaline opal as cavity fillings.

The complete lack of transitional flows between the Picture Gorge and Yakima types is noteworthy, and so is their separation in time. The conclusion seems inescapable that on the Columbia River plateau two distinct and separate batches of magma were poured forth in volume from different magmatic hearths at different periods of time. Yet the differences are of a kind that could be approximated by selective removal of early crystallizing plagioclase, olivine, and magnesian pyroxene from the Picture Gorge magma. The case against the Yakima type's being a differentiate from the Picture Gorge type is chiefly the lack of transitional rocks between them. Noteworthy, too, is the rarity of porphyritic flows of Yakima basalt, indicating that the parent magma had not undergone a long and complex crystallization history prior to extrusion.

TABLE 8

Modes: Klickitat River section (no. 10) of the Columbia River basalt

Specimen number	Plagioclase	Mono-clinic pyroxene	Olivine (including saponite)	Glass	Chlorophacite (including decomposition products)	Opakes
10-1	40.4	43.4	5.6	2.6	1.8	6.6
10-2	45.4	36.8	5.0	8.0	1.6	3.2
250 feet of sedimentary rocks (Ellensburg equivalent)						
10-4	45.6	20.6	3.2	18.0	5.4	7.2
110 feet of sedimentary rocks (Ellensburg equivalent)						
10-5	42.6	25.4	1.0	23.0	0.8	7.2
40 feet of sedimentary rocks						
10-6	49.0	19.8	4.8	21.6	0.8	4.0
10-7	45.4	34.8	none	8.2	5.6	6.0
10-8	41.2	33.0	none	14.0	6.4	5.4
10-9	39.8	21.2	none	31.4	2.2	5.4
10-10	36.2	27.0	none	25.0	8.0	3.8
10-11	37.4	28.6	none	32.6	0.8	0.6
10-12	37.8	26.4	0.4	26.0	4.8	4.6
10-13	44.6	33.6	1.0	13.0	5.6	2.2
10-14	47.8	33.0	1.4	6.2	8.8	2.8
10-15	31.2	19.2	none	44.8	0.2	4.6
10-16	31.4	16.8	none	51.8	none	(in glass)
10-17	43.4	36.8	none	9.4	5.0	5.4

LATE TEXTURAL AND MINERALOGIC VARIANT OF THE YAKIMA BASALT

In the southwestern part of the lava field, chiefly along Columbia River and in the area lying west of Columbia River between Wenatchee and Pasco, a textural and mineralogic variant of the Yakima basalt appears, which seems to have had a slightly different crystallization history than normal Yakima flows. It is characterized by a coarse but open network of large plagioclase microlites and of granular to elongate clinopyroxenes. The large plagioclase microlites have well-developed 010 faces but show ragged skeletal ends—a feature that was also noted by Wilkinson (Wilkinson, Lowry, and Baldwin, 1946, p. 20) in the Columbia River basalt west of the Cascades. Filling the openings between these coarse tangled microlites are patches of glass, varying from 1 to 4 millimeters in diameter (pl. 2-C). In most flows this glass has partly crystallized, and is half filled with flamboyant variolitic sheaves of feldspar needles and with a titaniferous opaque in large skeletal growths (pl. 2-D).

Pahoehoe tops and flow unit separations are more common in these flows than in the normal Yakima basalt. They also show a higher content of vesicles. In some flows, moreover, the glass mesostasis does not completely fill the voids between the large feldspar microlites but leaves a complicated maze of interconnected microlitic cavities. This microlitic texture is transitional to the coarse diktytaxitic texture (Fuller, 1931b, p. 116) so common in the olivine-rich basalts of the Cascade Mountains and southern Oregon plateaus. On weathering the interstitial glass is the first thing to decompose; weathered rock strongly resembles diktytaxitic-textured olivine basalt, but the mineralogy is quite different.

Older flows of this textural type (represented by flows 10-5, 10-9, and 10-12 to 10-14 in table 8) vary only slightly from normal Yakima flows in mineral composition, although they do contain a little more olivine (generally 0.5 to 3 percent), and a distinctly higher ratio of plagioclase to pyroxene than the normal Yakima basalt. But near the top of the sequence several flows containing 5 to 15 percent of olivine are interstratified with the less olivine flows. These have more normal textures, and less glass. Some contain pigeonite as the groundmass pyroxene. Modes of 14 of these flows are given in table 9, and 3 more (specimens 10-1, 10-2, and 10-6) are in table 8. The flows richer in olivine are among the youngest of the Yakima basalt; some are interstratified with the overlying Ellensburg formation. Even those that occur below the Ellensburg are commonly interlayered with thin interbeds of arkose, siltstone, and diatomite, or they show ancient soil zones and other evidence of weathering between flows. Some interbeds consist of coarse sand and gravel derived from a metamorphic-plutonic terrain. This indicates that stream gradients were being steepened by warping of the plateau at the time these late olivine flows emerged.

Some of the late olivine flows are confined to synclines that apparently were just beginning to form when these flows were erupted. Examples are: (A) Two flows that overlie beds equivalent to the Ellensburg formation in the Klickitat section (number 10), modes of which are given in table 8, specimens 10-1 and 10-2. (B) Several late flows that occupy the axial part of a syncline followed by Columbia River in the Arlington-Roosevelt area. Two of these flows lie above sediments equivalent to the Ellensburg formation. Others lie below the Ellensburg but contain intercalations of diatomite and micaceous sandstone. Modes of 4 of these flows are given under samples 1 to 4 in table 9. (C) The topmost flows in the axial part of the same syncline at The Dalles, Oregon. One of these flows, well exposed in the northwest part of The Dalles, was chemically analyzed by Washington (1922). The analysis is listed in column 1, table 4, and a mode from a thin section of this flow is listed as sample 13 in table 9.

Although most of these olivine flows are found in the southwestern part of the lava field, they occur elsewhere. The chemical analyses (columns 2 and 3 of table 4) given by Becraft and Weis (in press) of two basalts from the Turtle Lake quadrangle near the northeastern margin of the basaltic plateau are of this type of rock. Becraft (written communication) reports that the analyses are of the topmost flow of Yakima basalt in each area, and he kindly

TABLE 9

Modes: Late Yakima and Ellensburg flows, Columbia River basalt

Location of Samples	Plagioclase	Monoclinic pyroxene	Olivine (incl. saponite)	Glass	Chlorophacite (including decomposition products)	Opakes	Zeolites
1. 2½ mi NE Roosevelt, Washington	43.0	19.3	10.4	10.1	5.9	8.9	2.4
2. Top flow Yakima basalt, Wood Gulch	46.7	24.4	12.1	4.9	6.3	5.0	0.6
3. Rock Creek, Goodnoe, Washington	45.0	25.1	9.0	10.7	2.8	6.8	0.5
4. Rock Creek, Goodnoe, Washington	42.7	26.3	6.3	11.7	5.0	7.6	0.4
5. 5 mi S of Mabton, Washington	42.1	26.4	10.6	9.0	3.6	7.4	0.9
6. Roza flow, Selah Tunnel, Yakima, Washington	43.6	19.4	12.4	14.8	2.4	7.4	none
7. Wenas flow near Pomona, Washington	34.2	25.6	7.0	22.2	1.6	9.4	none
8. Platy flow, Frenchman's Springs, Washington	39.6	27.4	6.6	16.8	0.3	7.7	1.6
9. 2 mi NE Frenchman's Springs, Washington	50.1	22.0	12.5	5.5	2.4	7.0	0.5
10. Babcock Ridge, Quincy, Washington	34.6	21.4	8.0	27.7	1.4	6.9	none
11. Rock Island, Washington	31.6	23.8	5.2	31.0	trace	8.4	none
12. Turtle Lake quad (Becraft, in press)	39.1	21.3	5.6	24.7	0.9	8.2	none
13. The Dalles, Oregon	39.8	24.0	3.2	23.0	4.8	6.2	none
14. Intracanyon flow, Clarkston, Washington	42.4	36.0	6.8	8.4	1.4	4.6	0.4
Average	41.0	24.5	8.3	15.7	2.8	7.2	0.5

lent a thin section cut from one of the analyzed rocks. The mode listed as sample 12 in table 9 was made from this thin section. Another olivinic flow of Late Yakima type (mode listed as sample 14, table 9) is well exposed west of Clarkston, Washington. This flow was extruded after uplift and considerable erosion of the normal Yakima basalt, for it half fills a deep canyon cut in Yakima flows by an earlier stage of Snake River (Lupher and Warren, 1942). Another olivinic flow caps 250 feet of sedimentary rock that rest on top of Yakima basalt east of Buford Creek in Wallowa County, Oregon.

One of the two kinds of Stayton lava (see column 4 of table 4), reported by Thayer (1937) from the west side of the Cascade Range near Salem, Ore-

TABLE 10
Chemical analyses and modes: typical Quaternary olivine basalts

	1	2	3	4	5	6	Average
SiO ₂	48.71	49.0	49.38	49.44	49.6	49.95	49.35
Al ₂ O ₃	16.92	14.7	16.92	16.85	16.0	16.81	16.37
Fe ₂ O ₃	3.49	6.0	1.05	5.05	1.3	3.39	3.28
FeO	7.65	4.2	8.82	5.58	9.9	6.72	7.15
MgO	7.98	8.2	8.56	7.25	7.4	8.60	7.98
CaO	9.68	11.0	9.80	9.15	9.6	8.79	9.34
Na ₂ O	2.96	2.5	3.10	3.25	3.3	3.01	3.02
K ₂ O	0.40	1.8	0.40	0.66	0.53	0.49	0.71
H ₂ O ⁺	0.22		0.04	0.25		0.38	
H ₂ O ⁻	0.18	0.54	0.05	0.26	0.18	0.22	0.39
TiO ₂	1.38	1.3	1.40	1.80	1.5	1.21	1.43
P ₂ O ₅	0.22	0.59	0.19	0.39	0.34	0.17	0.30
MnO	0.18	0.18	0.17	0.17	0.20	0.16	0.18
CO ₂	0.02	0.26	0.01	0.01	<0.05	0.02	0.06
Sum	99.99	100	99.89	100.01	100	99.92	
Plagioclase	51.6	38.8	47.1	45.0	50.0	47.1	46.6
Pyroxene	17.7	30.6	20.4	26.0	19.0	22.1	22.6
Olivine	18.0	21.8	18.4	19.1	18.0	19.1	19.1
Glass	6.3	1.2	9.9	3.9	9.4	6.3	6.2
Chlorophaeite	none	none	0.9	none	none	none	trace
Opauques	6.3	4.0	3.3	6.0	3.6	5.3	4.8
		3.6(K.Spar)					
Zeolites	none	none	none	trace	none	trace	—
1. Porphyritic olivine basalt. Sec. 36, T 2 S, R 8 E, west of Black Lake, Hood River quadrangle, Oregon. V. C. Smith, analyst. USGS Lab. no. E2101. (new analysis) 2. Conant butte lava flow, Sec. 11, T 17 S, R 18 E, near Post, Oregon, P. L. D. Elmore and K. E. White, analysts. USGS Lab. no. 142180. (new analysis) 3. "Big Lava Bed," a recent flow. Lava Creek, Sec. 34, T 4 N, R 9 E, west of Willard, Washington. V. C. Smith, analyst. USGS Lab. no. E2093. (new analysis) 4. Postglacial olivine basalt flow, South Pine Creek, Hood River quadrangle, Oregon. Sec. 25, T 2 S, R 10 E. V. C. Smith, analyst, USGS Lab. no. E2100. (new analysis) 5. Top flow, olivine basalt, Ochoco State Park, 1 mile west of Prineville, Oregon. P. L. D. Elmore and K. E. White, analysts. USGS Lab. no. 142182. (new analysis) 6. Wind River lava flow, Trout Creek Hill, northwest of Carson, Washington. Sec. 7, T 4 N, R 7 E. V. C. Smith, analyst. USGS Lab. no. E2094 (new analysis)							

gon, appears to be identical in chemical and mineral composition, and also in texture, to these Late Yakima olivine flows.

Only a few chemical analyses of the late olivine basalts have been reported (table 4), but from them and the many modes that have been measured (tables 9 and 8), it is apparent that these rocks are lower in silica and notably higher in iron and titanium than normal Yakima basalt. They also show more variation among themselves, yet have a definite easily recognized consanguinity in chemical composition and mineralogy.

As to their source and origin, the more basic nature of these flows and their appearance during the waning stages of vulcanicity seems to rule out the idea that they are late differentiates of the Yakima basalt magma unless, perhaps, one assumes that the "chamber" which supplied the Yakima basalt was

so thoroughly eviscerated that the last final flows were clogged with crystal accumulates carried up with the final liquid dregs. But most of these flows are not strongly porphyritic. The few that are, such as the Roza flow of the Yakima-Vantage area, are so conspicuous that they are used as stratigraphic markers. Neither do these flows contain large glomeroporphyritic clots nor cognate inclusions of gabbro, troctolite, or similar rocks. In fact most are non-porphyritic and closely similar in appearance to the normal Yakima basalt. In their richness in olivine and plagioclase, the "Late Yakima" rocks show some resemblance to the widespread Pliocene-Quaternary olivine basalts that lie unconformably upon the Yakima basalt and spread over wide areas in the Cascade Mountains and central Oregon plateaus. The "Late Yakima" flows, however, are much less feldspathic and contain less than half the olivine found in these younger Pliocene-Quaternary olivine basalts (tables 9 and 10).

Could the accelerating tectonic movements that began in early Pliocene time have opened new fissures and brought the "Late Yakima" flows to the surface from a different, possibly deeper, site of magma generation than did the feeders for the main bulk of the Yakima basalt?

LATE STRUCTURAL MOVEMENTS AND ASSOCIATED OUTPOURING OF THE PLIOCENE-QUATERNARY OLIVINE BASALTS

This is not the place to discuss structural changes produced by isostatic movements connected with the withdrawal of vast volumes of magma from relatively few dike swarm centers, and the loading of the crust by lava in areas far removed from the feeders. That such movements did occur is suggested by the pronounced basining of the basaltic plateau. At the end of the period of extrusion the Yakima basalt must have had the form of a great plano-convex lens with its upper surface nearly flat, and its bottom a curve. Warping has continued until now the upper surface of the basalt stands from 2000 to well over 5000 feet above sealevel on all parts of its periphery (the extension of the Miocene basalts along the lower course of Columbia River west of the Cascade Mountains excepted). But in the central part of the plateau (Pasco and Umatilla basins) the surface of the basalt is still near sealevel.

How thick the basalt may be in the center of this great lens can only be conjectured. Nowhere except along the uplifted margins of the plateau has erosion bitten deeply enough to expose the floor on which the basalt was poured. Near the southeastern margin of the basaltic floods 3000 to 4000 feet of the Yakima basalt is exposed on the precipitous walls of the Snake, Salmon, Grande Ronde, and Imnaha River canyons. In some parts of this area another 1000 feet or more of Picture Gorge basalt lies unconformably below it. Sections of Yakima basalt over 2000 feet thick can be seen in the Columbia River gorge, where it crosses the Cascade Mountains, and also in the eastern foothills of the Cascades where rivers such as the Yakima have eroded deep water gaps through anticlinal ridges in the basalt (Smith, 1903b; Waters, 1955a). But all these thick natural sections are near the margin of the lens. The floor, where exposed, is a hilly to mountainous erosion surface with centripetal regional slopes. All the available evidence indicates that the basalt thickens rapidly toward the center of the plateau, but geophysical measurements are not available

to indicate the total thickness. One deep well drilled in Section 15 Township 11 North Range 24 East at the eastern end of the Rattlesnake Hills, not far from the center of the plateau, is reported to have bottomed in basalt at a depth of 10,655 feet.

As already noted, tectonic activity connected with the upheaval of the Cascade Range began to affect the western margin of the plateau during the waning stages of the outpouring of the Yakima basalt. Furthermore, faults of the Basin and Range province began to spread into the southern and southwestern margins of the lava field. Both folding and faulting grew in intensity during the Pliocene, raising the great east-west anticlinal ridges that characterize the western half of the plateau and breaking its southern part into a mosaic of fault blocks. The faults continue northward along the eastern slope of the Cascades, where they block out the east side of the upper Metolius and Hood River valleys, and extend far north of Columbia River into the Cascade Mountains of Washington.

Many of the Pliocene-Quaternary olivine basalts that cover great areas of the Cascade Range and that form the dominant rocks in the block-faulted plateaus of south-central Oregon rose to the surface along these faults. Although the younger olivine basalts were frequently confused with the Columbia River basalt in early reconnaissances, they are strikingly different in both field habit and mineralogy. At many places, moreover, they rest with strong structural unconformity upon upturned and eroded Columbia River basalt (pl. 2-A).

Many of the olivine basalts spread from fissure eruptions, but unlike the Columbia River basalt they also built numerous low shield volcanoes dotted with satellitic cinder cones. In places these shields are so closely spaced that they overlap. Some are lined up along major fissures: among the many examples are the NNW-SSE lines of basalt shields and cinder cones of the Simcoe Mountains in south-central Washington, and the lava shield and associated cinder cones that grew at the intersection of two faults south of the great bend of the Metolius River in the Cascade Mountains of Oregon. This shield fed the voluminous intracanyon flows of olivine basalt so conspicuous along the lower Metolius. Other centers of olivine basalt extrusion appear to be entirely independent of faults and fractures.

The Pliocene-Quaternary olivine basalts differ from the Columbia River flows in other ways than their mode of eruption. They occur in thin lava flows and flow units averaging less than 20 feet thick instead of the huge flows, averaging 77 feet thick, that characterize the Columbia River basalt. Many olivine basalt flows are complexly intertongued by filled lava tubes and narrow overlapping flow unit streams (Waters, 1960). Pahoehoe tops are common. Some flows spread out to smooth surfaces without either ropy tops or surface clinker. The most striking feature of their mineralogy is the high content of plagioclase and olivine, and the corresponding diminution in the amount of pyroxene (table 10). About half of them are light gray, and they show the characteristic open network of plagioclase laths with voids between (dikty-taxitic texture). Table 10 gives chemical analyses and modes of 6 flows of

olivine basalt collected from near the southwestern margin of the Columbia River basalts.

Because of these striking differences in field habit, mineralogy, (tables 6, 7, and 10), and chemical composition (table 5), and also because of their separation in time, it appears that the Pliocene-Quaternary olivine basalts did not arise as a differentiation product of either of the two major divisions of the Columbia River basalt. It is also interesting that olivine basalts of the same physical and chemical characteristics as the Pliocene-Quaternary olivine basalts reached the surface in the Hart Mountain area and other parts of southern Oregon during the Miocene at approximately the same times that the petrographically different Yakima basalt and Picture Gorge basalt was accumulating to the north (George W. Walker, personal communication). These regional relations appear to point to fundamental differences in either the depth, or else in the area of source of supply of the magmas, rather than to changes imposed on a single uniform molten mass during the course of its cooling history. Such suggestions are, of course, purely speculative, but as more data are accumulated about these interesting rocks we may be able to confine the speculations within a more rigorous framework. Present evidence, admittedly inconclusive, appears to favor the idea that the differences in the three types of lava that have been included in the Columbia River basalt, and also the difference between them and the olivine basalts of the Cascades and central Oregon plateaus, are to be sought in differences at the point of magma generation rather than as steps in the crystallization-differentiation of a single uniform parent magma.

STRATIGRAPHIC RELATIONS

We return now to a discussion of the stratigraphic relation of the two main divisions of the Columbia River basalt to one another, and to contiguous sedimentary formations.

From the evidence already outlined it is apparent that the "Columbia lava" of Merriam is somewhat older than the Yakima basalt of Smith. The two are separated both on the basis of chemical and mineralogical differences, and because of a structural unconformity between them. Moreover, the basalts that Merriam (1901, p. 303) described are not "the horizon which is most prominent along Columbia River" nor are they "that [series] of several to which the name [Columbia] is applied which has the greatest lateral extent, forming probably the greatest lava field in the world." Instead the basalt of the John Day basin seems to be restricted to areas of only moderate size which lie along the southeastern margin of the great area of flood basalts. It may, of course, have extensive underground extensions beneath younger lavas to the north, south, and west.

On the other hand Smith's claim (1901, p. 15) that the Yakima basalt is composed of "flood after flood of molten rock, which covered the vast area between what is now the crest of the Cascade Mountains on the west and the mountains of Idaho on the east, and between the mountains of northeastern Washington and the Blue Mountains of Oregon on the south" is confirmed.

To further restrict the name Columbia River basalt to the Yakima rocks, however, would only make additional confusion in an already confused termi-

nology. Since Merriam's time the basaltic rocks that he studied in the John Day basin have consistently been called the Columbia River basalt, and although Merriam did not designate a type section, the well-exposed section at Picture Gorge, Oregon has informally served as the type over the years. The present danger of confusion lies not so much in the use of the term "Columbia River" for these basalts as in the widely held but erroneous assumption that the rocks of the John Day basin are the time and mineralogical equivalents of the Yakima basalt to the north, plus the added fact that the Yakima basalt has also been considered as synonymous with Columbia River basalt in the literature. There is indeed good justification for such usage, since it was to this group of lavas that Russell (1893, p. 20-22) first applied the term "Columbia lava," and designated the canyons and coulees in Douglas County, Washington, as "typical."

These dilemmas in nomenclature are easily resolved if we elevate the *Columbia River basalt* to group status, and recognize two distinct formations within it: (1) The *Yakima basalt* as defined by G. O. Smith, and (2) the older basalts of the John Day Basin, called the "Columbia Lava" by Merriam, but herein renamed the *Picture Gorge basalt*, with the section at Picture Gorge designated as the type section. This nomenclature also provides the flexibility to add additional formations or other stratigraphic subdivisions as the need may arise, for, as will now be shown, there are still numerous stratigraphic problems which cannot be resolved until the entire Columbia River plateau has been geologically mapped.

GEOLOGIC AGE

At Picture Gorge, the Picture Gorge basalt is overlain by the Mascall formation of middle to late Miocene age (Merriam, 1901; Berry, 1929, p. 235; Chaney, 1925; Downs, 1956, p. 321-329; Chaney and Axelrod, 1959, p. 119-134). Farther northwest it disappears unconformably beneath the Yakima basalt of the Condon area.

The relation of the Yakima basalt to the Mascall formation is not clear, but at many points along its northern and eastern margin the Yakima basalt overlies, or is intercalated with, fluvial and lacustrine beds that carry an abundant Latah flora (Berry, 1929, 1931, p. 32; 1934, p. 101; Brown, 1937, p. 163-164; Chaney and Axelrod, 1959, p. 119-134). This middle or late Miocene flora is regarded by most paleobotanists to overlap that of the Mascall. The Ellensburg formation, first assigned to the Miocene, but now regarded to be early Pliocene on the evidence of both fossil vertebrates and the ecological relations of its fossil plants (Axelrod, 1950, p. 239-243) rests on the Yakima basalt at its type area, but also contains in its lower part some basalt flows (the Wenas basalt) that were considered to be the final outpourings of the Yakima basalt floods (Smith, 1903a). Moreover the uppermost flows of Yakima basalt are intertongued with sediments of the lower Ellensburg at many other localities in south-central Washington (Smith, 1904, p. 7; Waring, 1913, p. 19-21; Waters, 1955a, p. 670-673).

Below the base of the Ellensburg formation the Yakima basalt contains several interbeds of diatomite (Mackin, 1947). From one of these exposed in

a roadcut two and three-fourths miles north of Satus Pass in south-central Washington, Kenneth Lohman (*in* Sheppard, 1960, p. 10-13) reports 43 species of diatoms. The diatom flora indicates that this part of the Yakima basalt is of Early Pliocene age.

Bruce Foxworthy (Waters, 1955a, p. 664) has found fossils of fresh-water molluscs, tentatively identified as of Pliocene age, in sediments intercalated with the upper part of the Yakima basalt in Ahtanum valley west of Yakima.

The Latah formation and the Ellensburg formation consist chiefly of sediments of local derivation dropped by streams that were flowing from adjacent highlands toward the encroaching sea of basalt. These sedimentary rocks are now found as a discontinuous fringe that borders the basalt on the west, north, and east. Flows of lava repeatedly dammed the lower courses of the rivers, forming shallow lakes that spread over the margins of the lava plain and served as traps for fluvial and lacustrine sediments. Basalt flows from later eruptions entered and in many places completely over-ran these marginal lakes, building great pillow lava - palagonite complexes along the margin of the volcanic field (Fuller, 1931a). During the waning stages of volcanism, however, these relations were modified and even locally reversed. Many late flows did not spread the full distance from dike swarm to margin of the lava field, and still others were confined to deepening basins and to shallow synclinal troughs between growing anticlines.

The marginal interdigitation of the Yakima basalt flows with the sedimentary rocks of the Latah formation and lower Ellensburg formation suggests that the time of accumulation of the basal part of the Yakima basalt was somewhere in the range from middle to late Miocene, but the uppermost flows were erupted during the early Pliocene.

The age of the older Picture Gorge basalt can also be fixed within broad limits. At Picture Gorge this basalt lies unconformably upon the John Day formation (considered to be of Oligocene and early Miocene age) and is overlain by the middle to upper Miocene Mascall formation. This indicates a probable early or middle Miocene age for this section of basalt. We cannot be sure, however, that the basalt which lies unconformably beneath the Yakima basalt in the Imnaha canyon of northeastern Oregon is necessarily the precise age equivalent of that at Picture Gorge. Although similar in petrographic character it shows slight differences (table 6), perhaps indicating derivation from a different dike swarm. Petrographic similarity, moreover, is a very dubious criterion for the correlation of volcanic rocks.

Basalts considered to be part of the Columbia River basalt are widespread in the Lower Columbia valley west of the Cascade Mountains (Treasher, 1942; Wilkinson, Lowry and Baldwin, 1946; Lowry and Baldwin, 1952; Snively, Brown, Roberts, and Rau, 1958, p. 58-61). On the Washington side of Columbia River, Weaver (1937, p. 178-180) found these basalts to be interstratified with marine sandstones containing fossils of the Middle Miocene Astoria formation and Lowry and Baldwin (1952, p. 5) found the same relationship on the Oregon side. Moreover, they report (p. 3) the occurrence of two "varieties or phases" of the Columbia River basalt west of the Cascades, and Parke

D. Snavely (personal communication) reports a thick sandstone interbed separating two sequences of the Columbia River basalt north of the river.

Ultimately it may be desirable to extend the twofold division of the Columbia River basalt outlined in this paper to areas west of the Cascade Mountains. The terminology proposed gives the flexibility necessary to add further stratigraphic details. Meanwhile, until more of the Columbia River plateau and contiguous areas on the west and south are geologically mapped, we can have only an imperfect picture of the detailed distribution and age relations of the two basalt formations described herein to adjacent sedimentary formations. We need also additional information on the relations of the Columbia River basalt to the generally younger and more diversified sequences of olivine-rich basalt which spread over much of the Cascade Mountains, southeastern Oregon plateaus, and Snake River plain. When additional details have been supplied by field investigations and mineralogic work, we may have the basis for sound deductions regarding the fascinating problem of the relations between structural movements and magma generation during late Tertiary time in this tectonically and magmatically active province of the Pacific Northwest.

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More specifically, the division of the Columbia River basalts into two main petrographic types would have had to rest almost entirely on field evidence and on differences in the mode of the rocks if Donald H. Lindley, R. E. Wilcox, Thomas P. Thayer, George Becraft, and Warren Hamilton had not generously sent copies of unpublished chemical analyses of their specimens of Columbia River basalt to the writer, and permitted use of them in compiling the averages listed in tables 2, 3, 4, and 5.

Kenneth Lohman responded to the writer's request for an age determination of the diatomite from Satus Pass.

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MAPS OF CENOZOIC DEPOSITIONAL PROVINCES, WESTERN UNITED STATES

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ABSTRACT. Major provinces of Cenozoic deposits in western United States were controlled largely by the Cordilleran tectonic framework.

As in late Mesozoic time, the principal sites of Cenozoic aggradation were the eastern and western flanks of the Cordillera. In contrast, the axial part received limited deposits throughout much of Cenozoic time, except for accumulation of volcanic debris.

In early Cenozoic (Paleocene and Eocene) time, active aggradation prevailed along the western margin of the eugeosynclinal belt (thick marine deposits of the Pacific border) and in the Rocky Mountain miogeosynclinal belt (nonmarine deposits centered in Rocky Mountain basins and spreading across the northern Great Plains).

Middle Cenozoic (Oligocene to middle Miocene) time was marked by restricted flooding along the Pacific border and by widespread volcanic-rich nonmarine sedimentation in the central and northern Rocky Mountains and Great Plains. During this interval the axial part of the Cordillera was the site of extensive volcanic deposits—andesitic volcanic debris along the Cascade-Sierra Nevada axis, welded tuff in the Great Basin, and basaltic lava on the Columbia Plateau. Smaller patches of volcanic material accumulated in the Rocky Mountain miogeosynclinal belt.

During late Cenozoic (late Miocene and Pliocene) time submergence of the Pacific border was accompanied by deposition of thick marine sequences in actively sinking basins. An extensive volcanic-rich nonmarine mantle continued to accumulate across the eastern Cordillera. The axial part was also the site of widespread volcanic-rich nonmarine sedimentation in many newly formed basins.

INTRODUCTION

Much new information about Cenozoic deposits of western United States has been assembled in recent years. King (1958; 1959, p. 89-173) has published a fascinating synthesis of these data, but they have never been portrayed on paleogeographic maps. For this reason three maps (figs. 3, 4, and 5) of Cenozoic depositional provinces have been sketched as aids to students interested in the Cenozoic evolution of the vast region between the Great Plains and the Pacific Ocean. The pictures not only emphasize the remarkable extent of Cenozoic aggradation but they also reveal a continuity of depositional patterns within each of the principal provinces. At the same time, reading done for this project has pointed to a need for detailed studies of Cenozoic deposits like Mackin's (1960) fine work in southwestern Utah. Until more reports of this sort are available, an elaborate interpretation of the Cenozoic history of western United States is unwarranted.

No attempt was made to depict paleogeographic details of uplands, basins, and drainage patterns, or to draw isopachs. Instead, these maps simply show general provinces of deposition and their predominant lithofacies during early Cenozoic (Paleocene and Eocene), middle Cenozoic (Oligocene to middle Miocene), and late Cenozoic (late Miocene and Pliocene) time. In the Rocky Mountain region and along the Pacific border the larger persisting basins have been outlined. The extent of some provinces, such as the Great Basin, is misleading unless the reader recalls that there were many smaller basins in the area, especially in later Cenozoic time.

Any conclusions about the depositional history of these provinces must recognize the significant difference between accumulation of "normal" detrital

sediments in basins below local base level and the piling up of volcanic debris or the spread of volcanic ash quite independent of base level. For this reason most of the major volcanic fields are shown on the maps, although many of the smaller ones are not.

In selecting time intervals for summarizing Cenozoic events one risks distorting local patterns, especially by obscuring fluctuations during the interval. Allowance must be made accordingly. Moreover, inferred nondeposition is subject to error resulting from undetected erosion. The age and correlation of most of the stratigraphic units involved are recorded in Wood and others (1941) and Weaver and others (1944).

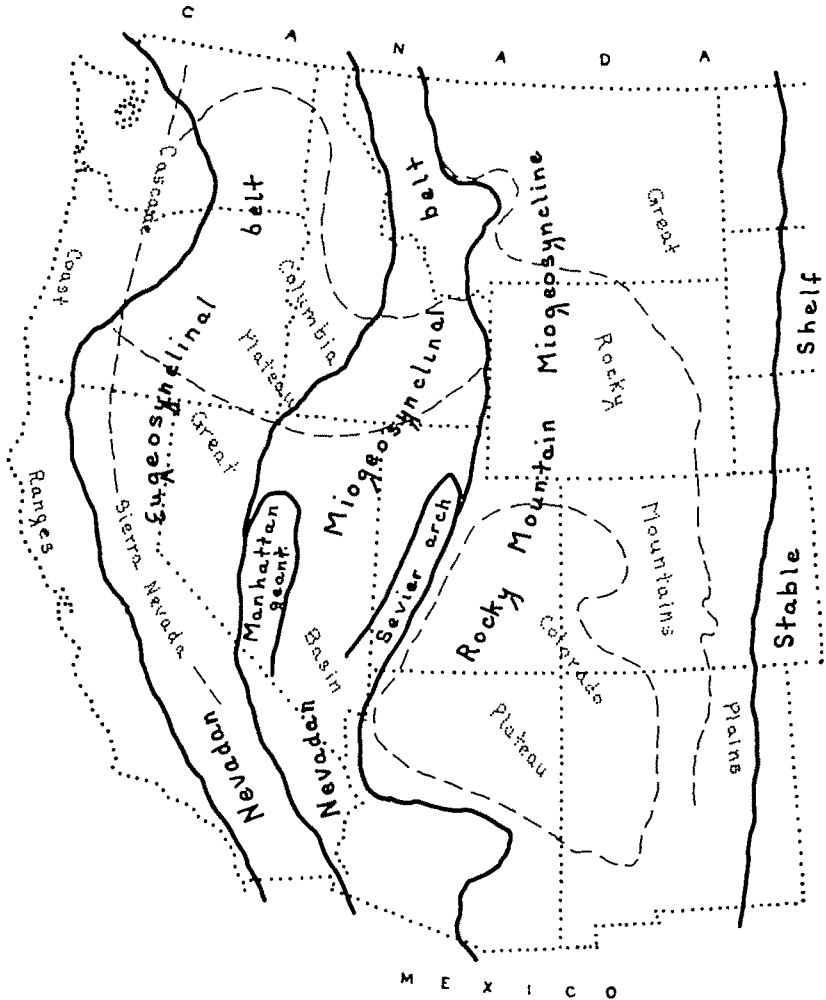


Fig. 1. Mesozoic tectonic and Recent physiographic provinces of the Cordilleran System, western United States (modified after King, 1958, fig. 4). Heavy lines and letters—tectonic provinces; dashed lines and dotted letters—physiographic provinces.

No references are cited in the text because most of the pertinent information is in the papers listed in the bibliography. Of all these I necessarily depended most on King's recent summary.

TECTONIC FRAMEWORK

Customarily, Cenozoic deposits in western United States are grouped according to the principal physiographic provinces (fig. 1). There is a more basic relationship, however, between Cenozoic depositional patterns and tectonic provinces of the Cordilleran System, as is evident on a paleogeologic map showing the distribution of older rocks beneath Cenozoic sequences (fig. 2).

In the west the Nevadan eugeosynclinal belt is flanked on its Pacific side by large basins in which marine aggradation was essentially continuous from Cretaceous to Cenozoic time, and in which it persisted throughout most of the Cenozoic era. Laterally, nonmarine deposits spread onto the Sierra Nevada-Cascade axis. Along the northern part of this axis andesitic volcanic debris accumulated almost continuously throughout Cenozoic time.

East of the eugeosynclinal belt, in eastern Nevada, central Idaho, and western Utah, a miogeosynclinal tract of unmetamorphosed Paleozoic and early Mesozoic rocks and a few patches of nonmarine Cretaceous rocks is bordered by linear positive areas, the Manhattan geanticline on the west and the Sevier arch on the east. Throughout this miogeosynclinal belt the cover consists mainly of middle and late Cenozoic deposits, and the material that accumulated here, as in the eastern part of the eugeosynclinal belt, comprises abundant volcanic debris. Only in the southeast, along the west flank of the Sevier arch, is there a terrane of early Cenozoic sedimentary rocks.

In the broad Rocky Mountain miogeosynclinal belt sedimentation near sealevel was essentially continuous from Cretaceous to Cenozoic time along the east flank of the Sevier arch, in large basins inherited from the Laramide orogeny, and on the Great Plains to the north. Unconformities may be present, but no large hiatus is involved. Moreover, aggradation accompanied by widespread volcanism prevailed in these areas throughout much of Cenozoic time. East and southwest of the intermontane basins late Cretaceous deposits apparently underwent erosion during early Cenozoic time. A positive area in southwestern Arizona underwent erosion throughout most of the era.

EARLY CENOZOIC AGGRADATION

During early Cenozoic time (fig. 3), as at the close of the Mesozoic era, the eastern part of the Nevadan geosynclinal belts was broadly arched, whereas the western margin of the Cordillera and the Rocky Mountain miogeosynclinal tract stood essentially at sealevel and were sites of widespread accumulation. Throughout the region a humid, warm temperate to subtropical climate prevailed.

External drainage from the relatively higher Cordilleran interior flowed westward across the low upland of the Sierra Nevada axis into the early Cenozoic seas flooding the Pacific border. Thick marine sequences that filled the string of large basins graded eastward across shallow shelves into nonmarine deposits and associated volcanic debris that accumulated at least locally on the Sierra Nevada core. Similar volcanic deposits also accumulated in the adjacent

western part of the Great Basin. To the north, on the eugeosynclinal tract, abundant volcanic debris spread across a coastal lowland and into marine basins along the northern Cascade and Coast Range belts. Here deposits several miles thick were interbedded with great masses of submarine lava. Some of these sediments apparently were deposited in deep water by turbidity currents.

In the eastern half of the Cordillera, Laramide orogeny in late Cretaceous and Paleocene time had outlined ranges in approximately their present form,



F.B. Van Houten, 1960

Fig. 2. Paleogeologic map showing generalized distribution of Paleozoic and Mesozoic rocks beneath Cenozoic sequences in the Cordilleran System. Gnarly pattern—metamorphic and plutonic rocks of Nevadan orogenic belt; dark dotted pattern—Paleozoic sedimentary rocks; light dotted pattern—Paleozoic, Triassic, and Jurassic sedimentary rocks; vertical lines—late Cretaceous sedimentary rocks succeeded by middle or late Cenozoic sequences; blank—late Cretaceous sedimentary rocks succeeded by early Cenozoic sequences; black patches—Laramide crustal blocks of eastern ranges of Rocky Mountains.

but they stood with summits no more than a few thousand feet above basin floors. Thick piedmont-valley flat, swamp, and lake deposits containing locally derived volcanic debris, filled differentially downwarped Laramide basins and extended northeastward across the northern Great Plains and westward along both flanks of the Sevier arch where lacustrine conditions were common. In most of the basins drab deposits of "coal-swamps" and lakes predominated in Paleocene time when the great Rocky Mountain seaway was destroyed. On the Great Plains to the east, however, a remnant of the seaway persisted into Paleocene time. In early Eocene time distinctive red-banded flood-plain and

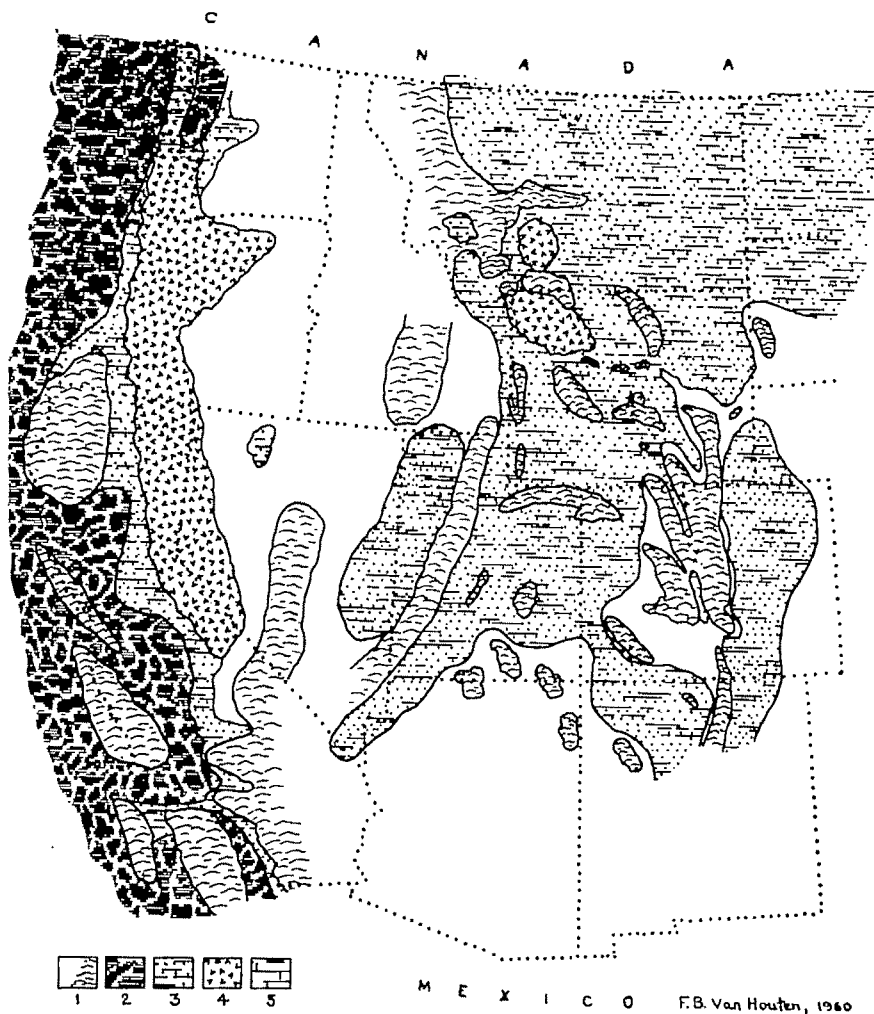


Fig. 3. Maximum early Cenozoic (Paleocene and Eocene) aggradation in western United States. 1) nondeposition and uplands; 2) predominantly marine deposits; 3) non-marine deposits; 4) predominantly volcanic debris; 5) predominantly lava flows—submarine basaltic flows in early Cenozoic interval, tholeiitic basaltic flows in middle Cenozoic interval, and varied flows and thin beds of welded tuff in late Cenozoic interval.

stream-channel deposits were widespread. As the region reverted to relative stability and differential movement between ranges and basins waned in later Eocene time, aggradation was limited to the major intermontane basins. Here the supply of detrital sediments has decreased and carbonate-rich deposits, including thick sequences of oil shale, accumulated in lakes which had outlets to the sea during most of their existence. Concomitant volcanic eruptions, many of which were a distinctive alkalic type, occurred throughout the area. By the close of this interval ranges of the central Rocky Mountains were deeply buried in basin-fill, producing a regional aspect of low general altitude, low relief, and subdued landscape.

MIDDLE CENOZOIC AGGRADATION

Throughout much of the Cordilleran System post-Eocene regional uplift and erosion interrupted aggradation and initiated distinctive conditions that characterized middle Cenozoic time (fig. 4).

Along the Pacific border the change was marked by a structural break-up of the early Cenozoic terrane and by regional uplift that restricted the spread of the sea, especially in the southern part of the province.

Vigorous volcanic activity along the Sierra Nevada-Cascade belt produced great masses of andesitic lava flows, mudflows, and pyroclastic deposits that built a low topographic barrier a thousand feet high. The volcanic debris also spilled over into the western part of the Great Basin which stood about 2000 feet above sealevel. Here some of it was trapped in newly formed fault basins. The deformation and volcanic accumulation apparently did not interfere with external drainage to the west or alter the climate significantly, however.

To the north volcanic debris from the Cascade eruptions contributed to the filling of the marine trough along the Coast Range belt while a broad non-marine basin in north-central Oregon was mantled with windblown ash. Then in early to middle Miocene time basaltic flows a mile or more thick spread across some 100,000 square miles in the northern part of the eugeosynclinal tract.

In the northern part of the Nevadan miogeosynclinal belt, nondeposition continued during mid-Cenozoic time except for a mass of lava and pyroclastic debris in south-central Idaho and ash-rich fluvial-lacustrine deposits, including oil shale, in a broad basin in northeastern Nevada. Moreover, this northern area of restricted aggradation was destined to be little disturbed during the late Cenozoic episode of intense block faulting in the Great Basin. In contrast, the southern half of the Nevadan miogeosynclinal tract and the flanking area to the east were buried beneath spectacular ignimbrites (welded tuffs) and associated lavas and pyroclastic debris which mantled a broad terrane of low relief. Ignimbrites many thousands of square miles in extent were "formed by nuées ardentes of incredible magnitude which swept with hurricane velocity across much of the Great Basin again and again during the post-orogenic period" (Mackin, 1960, p. 127). These older volcanic sequences were then widely faulted and mineralized during the first notable disturbance of the region, thus beginning the development of basin-and-range structure and topography.

When aggradation was renewed in the eastern part of the Cordillera in Oligocene time, deposits were laid down as widely as before, but the locus of sedimentation had shifted from the major Laramide basins to a wide belt that extended across the central Rocky Mountain province to the northern and central Great Plains. A significant proportion of this mantle was vitric ash and bentonitic mud produced by weathering of ash from frequent volcanic outbursts in the region to the west.

In contrast to the cessation of basin-sinking in the central Rocky Mountain region in Oligocene time fault-basins formed in the northern Rocky Mountains of Montana. Volcanic-rich sediments that accumulated here were similar to deposits that mantled the region to the southeast.

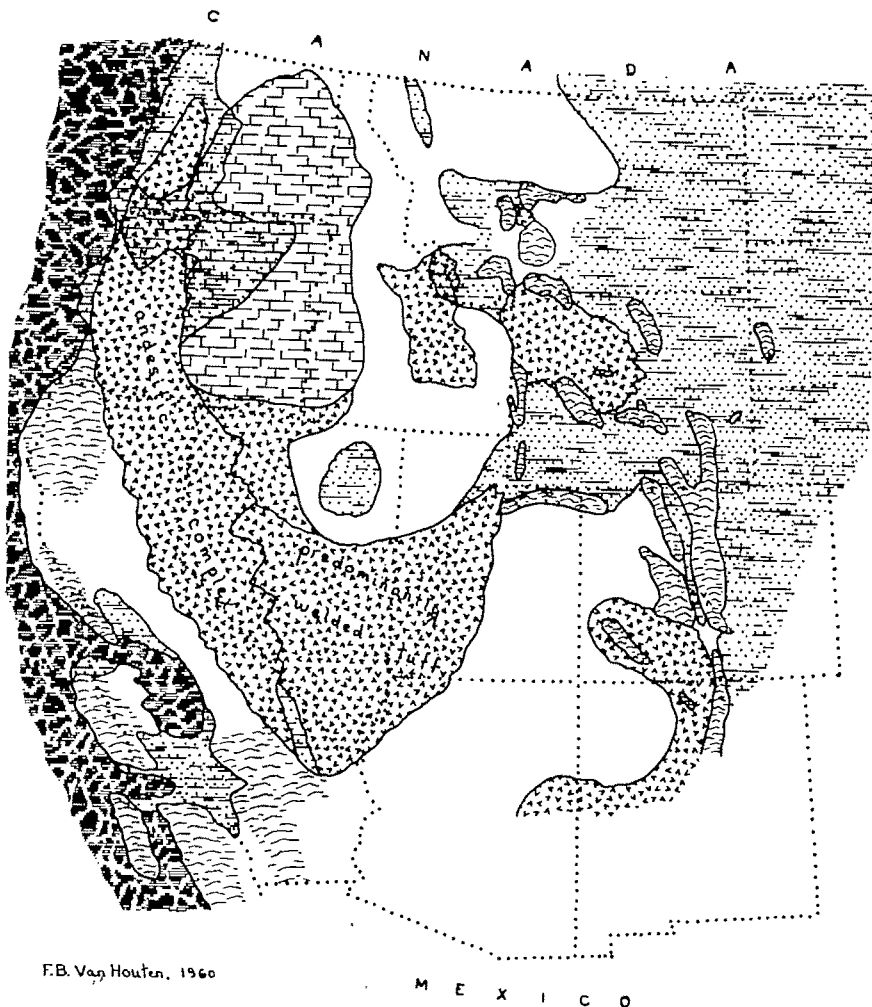


Fig. 4. Maximum middle Cenozoic (Oligocene to middle Miocene) aggradation in western United States. Legend—see fig. 3.

Nondeposition apparently prevailed in the southern part of the Rocky Mountain miogeosynclinal belt in mid-Cenozoic time, except in southeastern volcanic fields.

LATE CENOZOIC AGGRADATION

Late Cenozoic time was characterized by continued regional uplift and increased dryness, by widespread volcanic activity, and by extensive aggradation (fig. 5). Along the Pacific border faulting that outlined basins and ridges in their present configuration was accompanied by broad marine transgression. The thick sequences that accumulated contain abundant volcanic debris and in some of the more active basins they include deep-water turbidites.

Masses of volcanic debris from a score or more of great volcanic cones continued to pile up on the Sierra Nevada-Cascade axis, building the core to

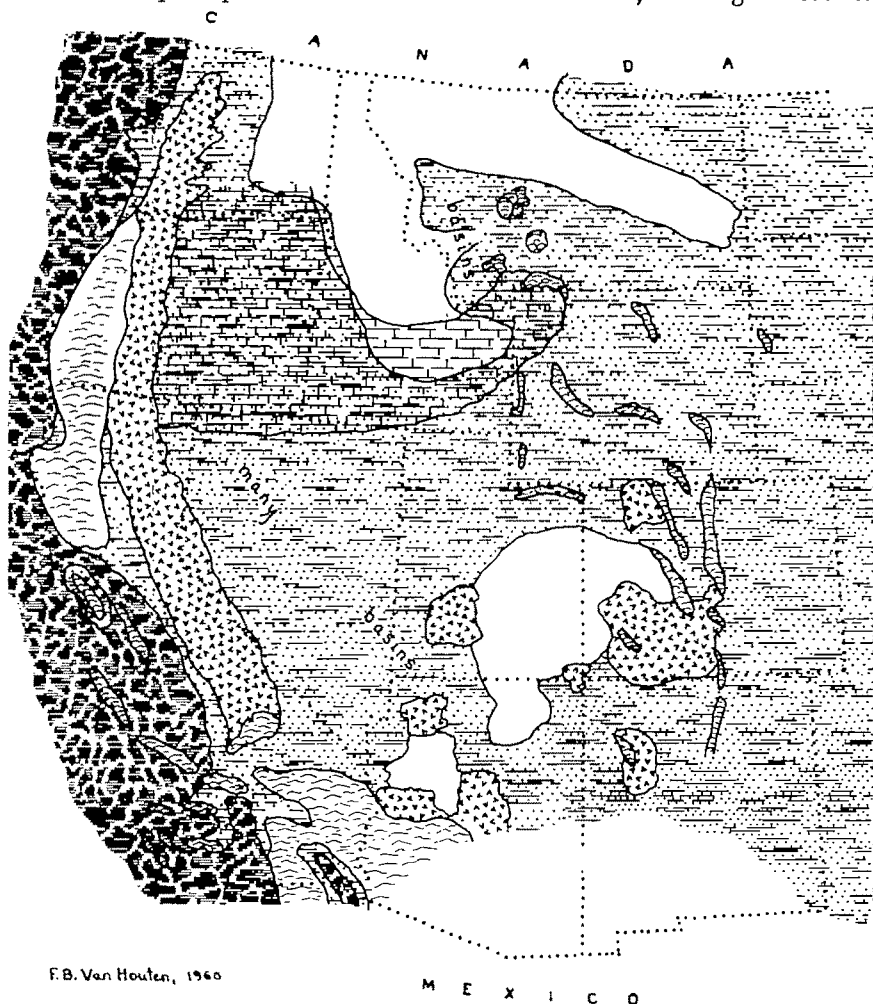


Fig. 5. Maximum late Cenozoic (late Miocene and Pliocene) aggradation in western United States. Legend—see fig. 3.

3000-4000 feet above sealevel and extending eastward into the Great Basin which lay about 1000 feet below the range crest. Not until Pliocene time was the range high enough to block external drainage from the Great Basin to the Pacific border.

During this interval the Columbia Plateau, the Snake River Plain, and the Great Basin formed a low plateau with scattered mountains and many lakes and swamps. Here fluvial and lacustrine basin-sequences with abundant siliceous and calcareous sediments and coarse locally derived conglomerate and volcanic debris, were interbedded with vitric ash that mantled the region. In this setting diatomite accumulated widely and much of the ash became zeolitized. To the north deposition of these volcanic-rich sediments was accompanied or followed by eruption of thin ash flows (welded tuffs) and extensive lavas of varied composition. In the Great Basin, where block faulting was active in late Cenozoic time, the volcanic-rich sediments accumulated in many separate but commonly connected basins, spread across faulted and tilted older Cenozoic rocks, and overlapped extensively on relatively low uplands.

Across the entire central and southern Rocky Mountain province and onto the Great Plains a nearly unbroken mantle of volcanic-rich flood-plain gravel, sand, and silt with scattered dunes and local algal ponds spread more widely than ever before in the Cenozoic era. In the northern Rocky Mountains volcanic-rich sediments continued to accumulate in intermontane basins. Non-deposition apparently prevailed only on protruding crests of the Rocky Mountain ranges and on the northern part of the Colorado Plateau.

SUMMARY

1. Cenozoic events in western United States were largely part of the postorogenic phase of mountain building.

2. The major provinces of Cenozoic deposits coincide with the basic tectonic pattern of the Cordillera.

3. As in late Mesozoic time the axial part of the Cordillera, and principally the Manhattan geanticline and Sevier arch and a positive area in southwestern Arizona, was the site of limited aggradation throughout much of Cenozoic time, except for the accumulation of volcanic debris.

4. As in late Mesozoic time the principal sites of deposition throughout Cenozoic time were the eastern and western flanks of the Cordillera where accumulation centered in large basins.

5. Along the western flank of the Cordillera downwarping and aggradation generally were more active in the north than in the south, and in the north volcanism dominated the scene throughout Cenozoic time.

6. Similarly, in the eastern part of the Cordillera and on the adjacent shelf to the east, extensive Cenozoic sedimentation began earlier in the north than in the south, suggesting somewhat greater regional uplift in southwestern United States after the Laramide orogeny. Progressively through the era sediments became coarser and thinner in the north. They overlapped on edges of ranges and encroached southward onto older rocks of the southern Colorado Plateau and the central and southern Great Plains, Presumably this resulted from relatively greater uplift of the northern part of the eastern Cordillera during successive stages of its regional elevation.

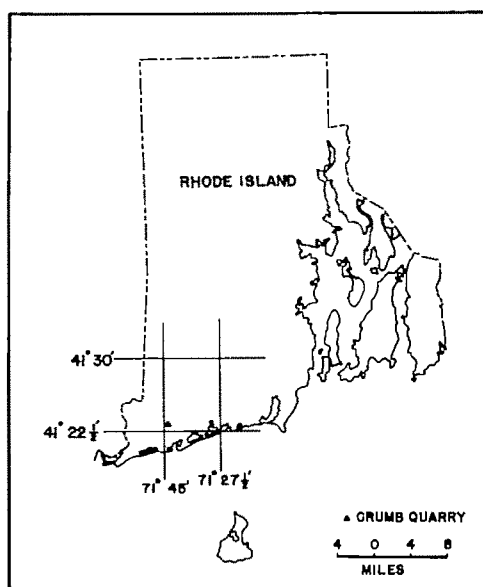


Fig. 1. Location of the Crumb Quarry in southwestern Rhode Island.

Quinn is gladly expressed. Though not always in agreement with the ideas proposed by the authors, his dissenting views, supported by long familiarity with the area studied, served to guide the authors in their reasoning and presentation of this study. Dr. Felix Chayes and Dr. Arie Poldervaart kindly read and criticized a preliminary draft of this manuscript.

The first author is indebted to Brown University for tenure of a University fellowship during the final semester of graduate study, without which much of this investigation could not have been done.

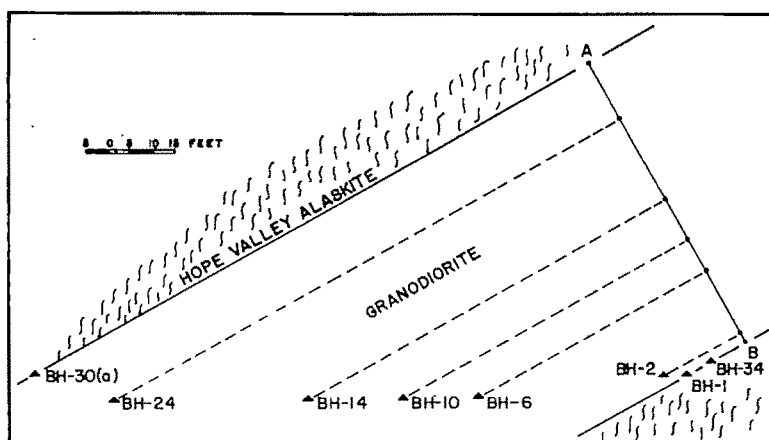


Fig. 2. Location of samples within the Bradford dike. Samples are projected to line AB to illustrate distance from contacts.

AGE RELATIONSHIPS

On the basis of field evidence the granodiorite dike under discussion appears genetically related to the Westerly granite (Chayes, 1950, p. 384) exposed in the Ashaway and Watch Hill 7½ minute quadrangle of Rhode Island. Petrographic evidence has also been advanced in support of such a relation (Quinn, 1953, p. 268), though it should be noted that real differences in bulk mineral composition do exist (Chayes, 1950, p. 384). Quinn and others (1957, p. 552) report the Westerly granite intrusive into the Narragansett Pier granite which in turn cuts folded and metamorphosed Pennsylvanian sediments of the Narragansett Basin. Lead-alpha age determinations for the Westerly granite (Quinn and others, 1957, p. 556) are in general agreement with stratigraphic evidence for a maximum age of late Pennsylvanian. Stratigraphic evidence for an upper age limit to the Westerly granite is lacking.

GRAPHIC AND STATISTICAL METHODS

Contoured scatter diagrams.—Contoured scatter diagrams have been prepared as done by L. H. Larsen (described in a personal communication). Points representing length and breadth of zircon crystals were plotted on arithmetic grid paper and counted within four ¼-inch squares defined by the medium-weight lines on K & E grid paper. The numbers are recorded at the center. This is repeated throughout the range of x and y, continually overlapping the squares counted, until a number has been recorded at each ¼-inch intersection. Contours are then drawn using any arbitrary interval. The contours represent only point density and not percent.

The reduced major axis.—The reduced major axis, one of several methods of fitting a straight line to a linear trend of points plotted arithmetically, was first described by Kermack and Haldane (1950), and its original application to the field of paleontology has been described excellently and in considerable detail by Imbrie (1956). Subsequently the reduced major axis has been used to represent length-breadth measurements for a given zircon population in the form of a straight line by Larsen and Poldervaart (1957), Taubeneck (1957), and Alper and Poldervaart (1957). The advantage of presenting data for a zircon population in the form of a straight line is that populations may be rigidly compared mathematically.

The derivation of the statistics $\bar{x}$ (mean length), $\bar{y}$ (mean breadth), a (slope of the reduced major axis), and the procedures for comparison of slope, position, and joint means of the reduced major axes follow the methods of Imbrie (1956), Larsen and Poldervaart (1957), Taubeneck (1957), and Alper and Poldervaart (1957). The statistics r (correlation coefficient), S_x (standard deviation of length) and S_y (standard deviation of breadth) were computed from the following short formulae presented by Dornbusch and Schmid (1955).

1.

$$\Sigma xy - \frac{(\Sigma x)(\Sigma y)}{N}$$

$$r = \sqrt{\left[\Sigma x^2 - \frac{(\Sigma x)^2}{N} \right] \left[\Sigma y^2 - \frac{(\Sigma y)^2}{N} \right]}$$

2.

$$S_x = \sqrt{\frac{\sum x^2}{N} - \left(\frac{\sum x}{N}\right)^2}$$

3.

$$S_y = \sqrt{\frac{\sum y^2}{N} - \left(\frac{\sum y}{N}\right)^2}$$

where N equals the number of zircon crystals measured. This method involves little chance for operator error and requires minimum time for calculation.

For comparison of position of reduced major axes, x_0 (Imbrie, 1956; Larsen and Poldervaart, 1957) has been arbitrarily chosen as .1333 mm, which fulfills the requirement that $x_0 > x_1$ and x_2 .

Following the procedure of Larsen and Poldervaart (1957), Taubeneck (1957), and Alper and Poldervaart (1957), the ends of the reduced major axis have been determined by dropping 2.5 percent of the zircon population at each end of the line.

In later sections the term "reduced major axis" will be abbreviated to R.M.A.

LABORATORY PROCEDURE

General statement.—The mechanical methods used to liberate heavy minerals in this study were designed to obtain maximum yield of heavy minerals and minimize breakage of zircon crystals, thus giving an unbiased estimate of the weight percentage of heavy minerals and the closest possible approximation to a true sample of the zircon population. After reviewing previous methods used to liberate zircon for work in correlation of felsic igneous rocks, it was concluded that not all of the zircons within a given sample were being freed by existing techniques and, therefore, that the resulting statistics might be biased. To test this idea, one aliquot (BH-34x) of a large sample was crushed until all of the material passed through 60 mesh. It was then subjected to a centrifuge separation on acetylene-tetrabromide, a magnetic separation, and finally a separation on Clerici solution of the nonmagnetic heavy minerals to obtain a pure concentrate of zircon. This concentrate was then compared with a concentrate of zircons, from a second aliquot (BH-34), liberated with the procedure used throughout this study.

This procedure departs from those previously used in that it entails repeated crushing of the sample. A 25-gram aliquot of a coarsely crushed (16 mesh) sample was sized into three fractions: (1) 80 to 170 mesh, (2) 170 to 250 mesh, and (3) < 250 mesh. The material was frequently sieved to avoid unnecessary breakage of already freed zircon crystals. Nonmagnetic heavy minerals (s.g. > 2.95) from the 80 to 170-mesh fraction were concentrated in a preliminary gravity separation and magnetic separation and then set aside. Following this the light minerals and magnetic heavy minerals from the preliminary gravity and magnetic separations were crushed to pass through the 170-mesh sieve, thereby freeing any finer zircons contained in these mineral phases. The procedure was repeated for the 170 to 250-mesh fraction and a similar separation performed on the <250-mesh fraction after all rock material except the nonmagnetic heavy minerals from the two coarser fractions

had passed through 250 mesh. The nonmagnetic, heavy fractions from the three fractions were then combined and subjected to separation on Clerici solution. The weight percentage of zircon in the residue indicates the increased effectiveness of the procedure used.

	BH-34	
zircon	0.078%	(

Visual comparison of R.M.A.'s in figure 3 indicate they compare extremely well in slope and position but differ slightly in $\bar{x}$ and $\bar{y}$. This is confirmed by Z values listed in figure 3. The aliquot crushed only through 60 mesh (BH-34x) has more zircon in the rock; hence the statistical parameters $\bar{x}$ and $\bar{y}$ are slightly different in slope and position, the two essential elements of the Poldervaart, 1957, p. 956), are not significantly altered. Close approximation to true values of $\bar{x}$ and $\bar{y}$ are suggested by the lines above should be used.

Mounting of zircons.—All zircons were mounted in a refractive index of 1.54. The zircon concentrates from all samples discussed below) were mounted on a single slide. In the sample BH-34 (fig. 2), which yielded over 50,000 doublets, the great number of crystals present prevented the good distribution of the population on the slide. This results in differences in the parameters calculated from two separate aliquots each involving 200 zircons in field grids spaced so as to cover the slide. This difficulty was overcome by measuring a large number of zircons. A zircon count of 800 crystals compared favorably with a count of 400 crystals. The raw data of all 1200 counts were used to determine the statistics for the sample.

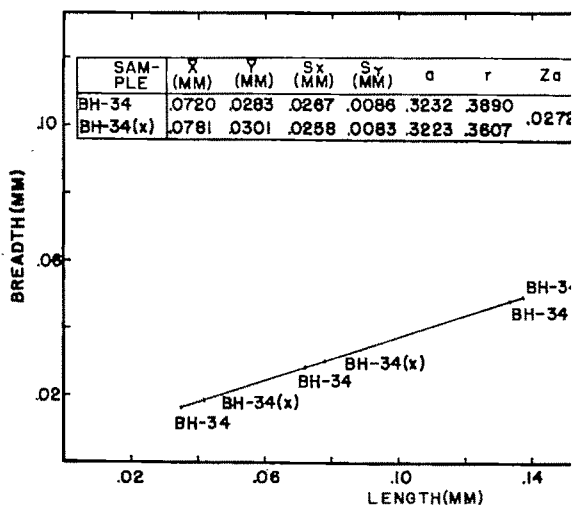


Fig. 3. Reduced major axes and statistical parameters of the same sample freed with two different techniques.

TABLE 1
Parameters for two counts of sample BH-34

Sample	$\bar{x}$ (mm)	$\bar{y}$ (mm)	S_x (mm)	S_y (mm)	a	r_1
BH-34 (N = 800)	.0709	.0283	.0263	.0086	.3257	.3320
BH-34 (N = 400)	.0742	.0283	.0273	.0088	.3233	.5017
Slopes Compared	Positions Compared		$\bar{x}$ Compared		$\bar{y}$ Compared	
Z_a	Z_p		$Z_{\bar{x}}$		$Z_{\bar{y}}$	
.1347	1.1414		1.5611		0.0000	

Because of the difficulty described above with sample BH-34, it was decided to split the zircon concentrate from a second bottom contact sample, BH-1 (fig. 2). As Larsen and Poldervaart (1957, p. 551) had already shown that the cone and quarter method of reducing sample size introduced significant errors, a different approach was adopted. This consisted of mixing the zircon concentrate thoroughly with a relatively large portion of clean, crushed, and sized glass, and splitting the mixture with a #212 Aepor micro-splitter. Each half was freed of glass by gravity separation on Clerici solution and mounted separately. The parameters shown in table 2 for each slide indicate that this method is also unreliable. The raw data from each slide were combined to determine the statistics for the sample.

TABLE 2

Statistical parameters of zircons from two halves of a split concentrate (BH-1)

Sample	$\bar{X}$ (mm)	$\bar{Y}$ (mm)	S_x (mm)	S_y (mm)		
BH - 1(a)	.0867	.0345	.0310	.0106		
BH - 1(b)	.0924	.0335	.0335	.0090		
Sample	a	r	Z_a	Z_p	$Z_{\bar{x}}$	$Z_{\bar{y}}$
BH - 1(a)	.3433	.3390	2.5815	4.6490	1.7747	1.0068
BH - 1(b)	.2681	.2967				

Measurement of zircons.—Measurements of length (x) and breadth (y) for at least 200 zircons were made for each sample. A magnification of $372\times$ was used, and only those doubly terminated zircons falling within the microscope field were measured. The fields were uniformly distributed over the entire slide.

PETROGRAPHY, ZIRCON DESCRIPTION, AND FIELD OBSERVATIONS

Petrography.—Modal analyses for samples of Westerly granite from the dike at Bradford, given by Quinn (1943, p. 279) and Chayes (1950, p. 384), show the rock to be a granodiorite. In order of decreasing abundance the major constituents are oligoclase (An_{18-22}), microcline, quartz, and biotite. The accessory minerals are allanite, apatite, magnetite, sphene, and zircon.

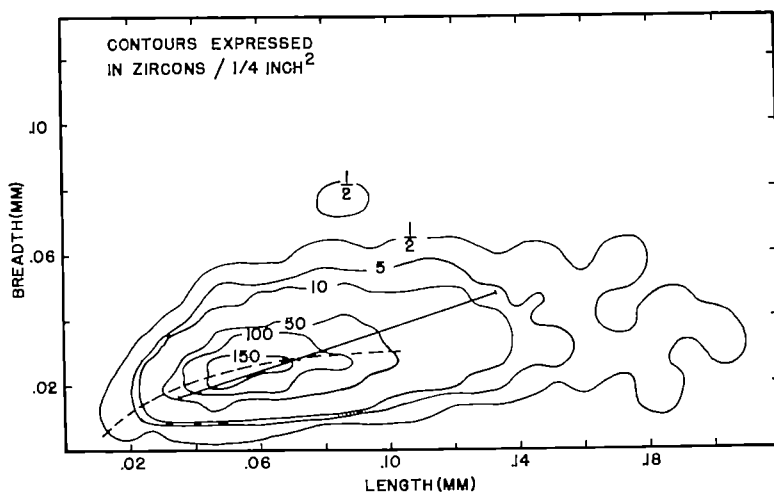


Fig. 4. Contoured scatter diagram, reduced major axis, and visual growth trend (dashed) for 1200 zircons from sample BH-34.

Pyrite, rutile, fluorite, and monazite are present in trace amounts. From textural relations Quinn (1943, p. 276) finds the order of crystallization of the main constituents to be: biotite, oligoclase, microcline, and quartz, with the accessory minerals, allanite, apatite, zircon, most of the sphene, and some of the magnetite forming early.

Ring (1952), using stained thin sections representing all parts of the dike, found no systematic variation of the main mineral phases.

Orientation of biotite has been observed in thin sections at various elevations in the dike. A roughly parallel arrangement also has been observed in dark streaks of heavy minerals in the upper and lower contact zones.

Description of zircons.—The zircons are extremely clear, varying considerably in number and type of inclusions which take the form of: (1) thin, colorless prisms, (2) reddish brown isotropic grains of irregular shape, (3) small, euhedral, zircon-like crystals, and (4) indistinct aggregates of fine, dark particles. The development of first- and second-order prisms, $m(110)$ and $a(100)$, terminated by first- and second-order pyramidal faces, $p(111)$ and $e(101)$, is common. Basal pinacoids, $c(001)$, and the steep pyramidal faces, $u(331)$, are less common. In general the development of crystal faces is good, though the junctures between crystal faces do not usually appear sharp under high power (372 $\times$). Hence numerous crystals seem slightly rounded even under high magnification. However, in most cases the crystal faces are completely intact, which suggests that the lack of sharpness at the intersections of some faces may be due to the presence of other more gently inclined faces not visible to the observer. Zoned crystals are rare and occasionally the broken end of a crystal is overgrown with somewhat lighter material.

The coefficient of correlation, r , for the zircon populations ranges from .1753 to .3958 with a mean value of .2909 (fig. 5). Alper and Poldervaart (1957, p. 962) give a mean r value of .74 for the zircons of the Bald Moun-

tain batholith and a mean r value of .62 for those of the Animas stock, and suggest that the smaller value results from more rapid crystallization or more variable conditions (P,T). In the case of the zircons from the Bradford, Rhode Island, granodiorite dike the small mean value of r may have a similar origin. However, another possibility should be considered.

When 1200 measurements of length and breadth for sample BH-34 are plotted and contoured, a curvilinear trend is suggested (indicated by the broken line in figure 4), primarily by the smaller zircons. This is not apparent on a scatter plot of only 200 zircons for this sample or others reported in the literature. Thus, it may be that both the small value of r and the curvilinear trend exhibited by the smaller zircons, together with the very small size of the zircons in the dike, are characteristic of an "immature" zircon population. The early-formed curvilinear trend defined by small crystals is lost upon attainment of "maturity" by populations with longer crystallization histories.

Field observations.—Megascopically the granodiorite dike appears very uniform in its mineralogy and texture, except for narrow zones at the upper and lower contacts.

The bottom contact is approximately planar, exhibiting some smooth, undulating irregularities with a maximum magnitude of two to three feet (Quinn, 1943, p. 275). In general an increased amount of heavy minerals is quite common; and, although there is generally only one layer present over any particular bottom area, as many as three have been observed together, each separated by approximately one inch. In several instances these layers are observed to be continuations of dark concentrations on gentle rises in the lower contact, and in one such case the layer extends for many feet straight

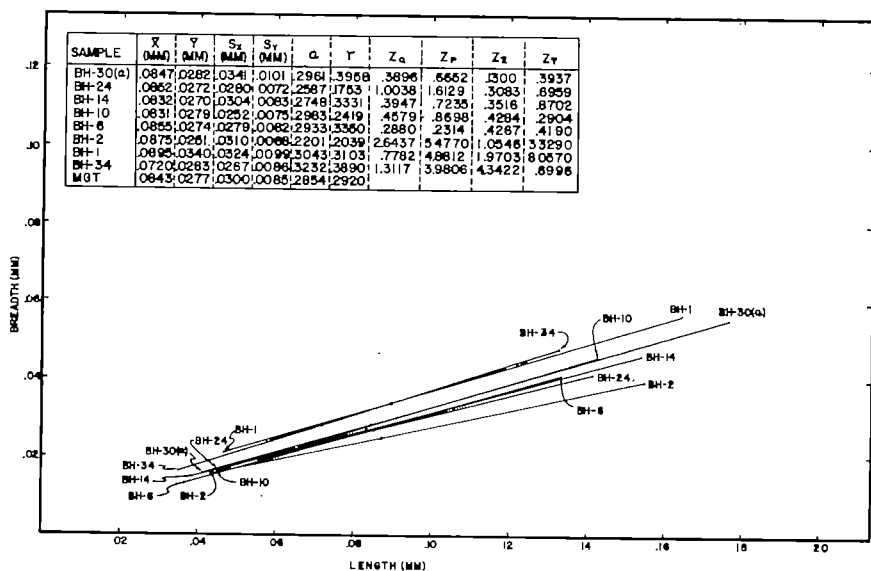


Fig. 5. Reduced major axes and statistical parameters of zircons for all samples. Comparison of each sample is made to the mean growth trend (M.G.T.).

over a depression (rather than following the contour of the depression), devoid of excess dark heavy minerals along the contact.

The contact is also characterized by protuberance of numerous large feldspar crystals probably formed by recrystallization of the underlying Hope Valley alaskite in a thin ($\frac{1}{2}$ inch) zone immediately below the contact. In thin section the tops of protruding mineral phases are quite free of heavy minerals relative to the depressions between them, the heavy minerals appearing to have been swept off by moving magma. The same feature is seen in hand-specimen (Quinn, 1943, fig. 3, p. 275).

The plane of the upper contact is likewise regular, but displays a zone of variable width (1 to 3 feet) characterized by increased grain size, local development of pegmatitic texture, increased muscovite content (Quinn, 1943, p. 276), less biotite locally, and layers with concentrations of heavy minerals.

Balk (1937, p. 113 and 115) has reported the occurrence of disconformable platy and linear flow structures in the granodiorite dikes occurring in the vicinity of Westerly (five miles southwest of Bradford), Rhode Island. The authors have also observed disconformable platy flow structures in the Crumb quarry, defined by steeply dipping flakes of biotite with an approximate northwest trend. This was observed in the contact zone as well as the main body of the dike. However, all observed platy flow structures within a few inches of the contact are oriented approximately parallel to the contact plane.

RESULTS

During this investigation two principal mechanisms have been examined in an effort to account for variations in heavy minerals vertically through a granodiorite dike. The two mechanisms considered were gravity settling with accumulation primarily along the lower contact; and formation of schlieren, causing concentration of early-formed heavy minerals in thin layers in the contact zone and along the contact plane. Results derived from both laboratory and field studies have caused the authors to favor the latter explanation, though gravity settling on a very small scale early in the emplacement phase of the dike cannot be ruled out categorically. The basis for this conclusion is considered below.

TABLE 3

Weight percentage data for heavy minerals*

Sample	BH-1	BH-34	BH-2	BH-6	BH-10	BH-14	BH-24	BH-30(a)
Zircon	.057%	.078%	.033%	.030%	.022%	.035%	.029%	.027%
Sphene, Apatite	.237%	.201%	.130%	.146%	.133%	.317%	.104%	.095%
Biotite, Allanite	6.208%	2.892%	3.835%	2.595%	2.773%	1.887%	2.706%	1.600%
Magnetite	1.301%	.796%	.774%	.882%	.844%	.251%	.887%	1.150%
Total Heavies	7.801%	3.967%	4.772%	3.653%	3.772%	2.490%	3.726%	2.882%

* The weighing procedure and original sample size formally allow reporting to .00X percent. However, since none of the samples have been processed in duplicate, and the separation procedure is long and complicated, it may be more correct to round the data off to .0X percent. Note that this would not affect the discussion or conclusions in any significant way.

Table 3 summarizes the weight percentage data obtained in this study for seven levels (two samples are from the lower contact) in the dike. One of the most striking features exhibited by the weight percentage data is the essentially constant amount of zircon in all samples through the dike, exclusive of samples at the lower contact. Two samples from the lower contact (BH-1 and BH-34) show approximately a 2.0x- to 2.5x-fold increase in the quantity of zircon present, thus recording an abrupt, significant departure from the zircon content of all samples at higher levels.

Biotite, which is the major constituent of the heavy mineral fraction, shows the greatest variation in weight percentage, exhibiting neither pronounced uniformity nor systematic variation in its distribution. The extreme variability of the biotite content, coupled with the fact that biotite concentrations in schlieren are visibly present at the top of the dike, argue against gravity settling of this phase.

Combined weight percentage data for apatite and sphene show a pattern similar to zircon in the main body of the dike, whereas the increase at the bottom contact compared to BH-2, two and one-half feet above, is slightly less than the maximum variation (BH-14) in the dike. Magnetite is quite uniform throughout the dike with the exception of sample BH-14 and samples from the upper and lower contacts. Although both contacts show increased amounts of magnetite, it has been suggested by Quinn (1943, p. 279) that at least part of the magnetite at the contacts is due to migration of pegmatitic or hydrothermal solutions along the contacts. As it is impossible to determine the fraction of total magnetite due to possible enrichment, this phase cannot be used as a basis for interpreting weight percentage variations through the dike.

Weight percentages of total heavy minerals exhibit the same pattern defined by biotite. This is expected as biotite is the major component of the heavy mineral fraction.

Quinn (1943, fig. 3, p. 275) records a very characteristic feature of the lower contact, viz., large recrystallized mineral phases protruding from the rock material beneath the contact plane. These result in formation of troughs that are enriched in biotite and zircon relative to adjacent crests. On a much larger scale some of the broad, gentle depressions in the undulating lower contact are found to be completely free of abnormal amounts of biotite. Above one such depression are found sharply bounded, dark flow layers, which extend out from the crest of an adjacent rise. Here the absence of excessive amounts of heavy minerals in the gentle trough, and the very existence of thin, foliated, sharply defined layers over such depressions argue against gravity settling of heavy minerals before or after the formation of the layers. Similar flow layers are observed in the upper contact zone and in the same manner argue against appreciable settling after flow had ceased, as does the presence of disconformable platy flow structures in the main body of the dike (described above).

On considering the statistical parameters and R.M.A.'s (fig. 5) for the various samples through the dike, it is clear that all samples above the lower contact zone (i.e., exclusive of BH-1, BH-2, and BH-34) are identical (assuming a 95 percent confidence level). This is considered very strong diagnostic evidence against the occurrence of gravity settling, as sorting of zircons on the

basis of morphology would be a necessary consequence of such a mechanism.¹ It should be emphasized that the sorting effect of gravity settling, if it had occurred, would be best recorded in the upper contact zone, whereas the next most significant changes would be observed in the lower contact zone. Variations in the former are completely lacking (see BH-30(a), fig. 5), which argues against such a mechanism, whereas variations in the latter are considered more adequately explained in terms of sorting of the original zircon population during magma flow.

TABLE 4
Calculated mean volume of zircons in zircon populations

Sample	Mean Volume		
BH-34	approx.	58	10^{-6} cu mm
BH-1	"	103	10^{-6} " "
BH-2	"	55	10^{-6} " "
BH-6	"	64	10^{-6} " "
BH-10	"	65	10^{-6} " "
BH-14	"	61	10^{-6} " "
BH-24	"	63	10^{-6} " "
BH-30(a)	"	67	10^{-6} " "

Variations in the statistical parameters of the three lowermost samples will now be considered. The mean elongation ($\bar{X}/\bar{Y}$) for the two contact samples, BH-1 and BH-34, is 2.632 and 2.544 respectively, while above the lower contact zone the mean elongation values range from 2.982 (BH-10) to 3.132 (BH-24). Both samples also show greater values for the slopes of their R.M.A.'s than that of the average slope for the dike, thus indicating an increase in the number of more equant or less elongate zircons, although the slopes do not differ significantly from that of the mean growth trend (fig. 5). BH-1 is also characterized by an increased proportion of zircons having high volume values. This is shown in table 4 and by the point ($\bar{X}, \bar{Y}$) in figure 5, where both $\bar{X}$ and $\bar{Y}$ are significantly greater than $\bar{X}$ and $\bar{Y}$ of the mean growth trend (see $Z\bar{x}$ and $Z\bar{y}$, fig. 5). The process of gathering early-formed crystals in a thin layer adjacent to the contact plane, in such a manner as to relatively concentrate the less elongate crystals, can perhaps be inferred from the observations and data in hand. Magma moving past a slightly irregular stationary wall lost crystals to the indentations and the flow layers forming in the contact zone and against the wall. In such an environment the less elon-

¹ Differences in zircon elongation are reflected in differences in the slopes of R.M.A.'s; higher values of $\bar{X}$ indicating more equant crystals.

In the calculation of mean volumes, $\bar{V}$, for zircon populations (listed in table 4) the formula $\bar{V} = \bar{Y}^2\bar{X}$ was used, where $\bar{X}$ is mean length and $\bar{Y}$ is mean breadth, ignoring the presence of pyramidal faces. A small element of error is thereby introduced as the calculated volume will necessarily exceed the true volume, with the volumes of more nearly equant crystals being slightly more exaggerated than those of the more elongate ones. The error is of no consequence when differences between populations are large.

Differences in $\bar{V}$ are also shown by differences in the positions of points ($\bar{X}, \bar{Y}$) of the R.M.A.

gate crystals were more prone to remain behind in the indentations and flow layers forming in the contact zone. The concentration of early-formed heavy minerals in a thin layer against the contact surface is pictured as resulting from the same mechanism responsible for development of similar layers above the contact and bounded on both sides by granodiorite. This would result from the chance collision of crystals with each other and with protuberances from the irregular wall. Although the approach of two or more crystals is fortuitous, once they are sufficiently close to retard the movement of magma between them, the lamellae of magma will then flow around them, and opportunity for accumulating further solids is increased (Balk, 1931, p. 336). This process would operate most efficiently in areas where successive layers of magma have maximum velocity differences and minimum thickness. The net result is concentration of existing mineral phases in a layer along the contact and in flow layers above the contact, with selective concentration of the less elongate zircon crystals. The geometry of such crystals favors their remaining in a chance grouping of zircons (and other existing minerals) around which magma is flowing, whereas more elongate crystals would have greater opportunity to be picked up again and dragged along in the magma. The two contact samples under consideration appear in agreement with this explanation, and in addition indicate that lateral variations in volume frequencies can be expected. This latter situation would not be expected if concentration of zircon in an enriched contact layer were due to gravity settling.

Sample BH-2 is the only sample to record a statistically significant departure from the average slope for all samples through the dike, its lower value indicating an enrichment in the more elongate zircons. It is also significantly different in position and mean breadth. A rigorously reasoned explanation for the unusual character of this sample has not been developed, though a possible explanation is that BH-2 is a population from which the more equant crystals have been removed by formation of flow layers during emplacement. The selective removal of less elongate grains would result in a population similar to BH-2.

CONCLUSIONS

The following conclusions are drawn from this investigation:

1. Laminar flow has resulted in a sorting out of less elongate zircons into flow layers, megascopically defined by increased amounts of biotite, and has further differentiated these crystals laterally on the basis of size (volume).
2. Zircon populations used for characterizing a mass of felsic igneous rock material should be obtained from massive samples devoid of flow layering and preferably obtained well within the central portion of an intrusive. Samples involving flow layers cannot be relied upon to provide a representative sample of the total zircon population.
3. Comparison of zircon data determined by different investigators requires the mineral separation procedures used to be designed so as to assure that the concentrates are representative of all zircon sizes present. Significant differences in joint means result from use of separation procedures that do not meet this requirement, although the slope and position of the line fitted to the population remain constant.

4. Involvement of zircons with biotite in flow layers argues for the early formation of both minerals in felsic igneous rocks.

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CALICHE PSEUDO-ANTICLINES IN THE FITZROY BASIN, WESTERN AUSTRALIA

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ABSTRACT. An occurrence of caliche pseudo-anticlines is reported from the Limestone Ranges of the Fitzroy Basin. They compare closely with Mexican examples described by Price (1925), except that here they are developed entirely in competent limestones. Price stressed only the semi-aridity of the climatic conditions favorable to their development, but high temperatures are regarded as necessary also. The significance of these features for both the stratigraphic mapping and the geomorphological study of the area is illustrated.

The latest American dictionary of geological terms (American Geological Institute, 1959) defines "pseudo-anticline" in this way:

An arrangement of rock strata simulating the arch of an anticline. Used with reference to sand bodies which have a convex top (Ver Wiebe, W. A., *How Oil is Found*, 1951).

Though the first part of this definition may command general approval, there is room for criticism of the whole in that no reference is made to the prior usage of Price (1925), particularly since this usage differs from that of Ver Wiebe. Price employed the term for minor buckling of the superficial strata of limestone-sandstone-shale interbeds owing to the formation of caliche. It may be best to retain a broad connotation for "pseudo-anticline" (cf. German *Pseudo-dislokation*) and qualify it for specific types as is suggested in the title of this note.

Price described caliche pseudo-anticlines in the Mesa de Solis on the coastal plain of northeastern Mexico. He predicted that similar features would be found elsewhere in semi-arid lands where lithology would provide calcium and other salts in surface and ground waters and where joints or other planes of weakness permit the ready entry and movement of these waters. In keeping with this prognosis, the present writers report an occurrence encountered in a reconnaissance geomorphological study of the Limestone Ranges of the Fitzroy Basin during May-July, 1959 (fig. 1). The Limestone Ranges are developed on late Middle and Upper Devonian reef complexes (Guppy and others, 1958; McWhae and others, 1958, p. 42), characterized in lithology by a predominance of pure limestones, though dolomitization is by no means absent.

The pseudo-anticlines were found¹ on an almost flat pedimented surface east of the Geike Range and within the outcrop area of the Fossil Downs Formation, which in general is a sequence of calcarenites, clastic and biohermal limestones, in parts sandy and silty. Where the features occur, the beds are nearly horizontal in attitude and fine-grained pure calcarenites are exposed.

At the locality there is a group of low ridges, which are up to 5 to 10 feet high, 30 to 150 feet across, and up to several hundreds of yards in length. Along their lower flanks the ridges have slabs of bedrock tilted up to angles as steep as 30°, while the upper parts and crests consist of caliche, giving them

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¹ The precise location is about 4 miles north of Champagne Bore along the track from Fossil Downs Homestead to the J. K. Yard.

a blistered, cracked appearance. The wider troughs between (up to 150 feet across) are level-floored with frequent flat slabs of calcarenite outcropping; otherwise there are thin loamy soils and some caliche rubble. Where the ridges lie close together, the "synclinal" arrangement of the limestone is in places even more obvious than the "anticlines" of the ridges, though two ridges were seen to be almost entirely of bedrock showing scarcely any caliche. Some slabs show the transition to caliche, with fragments of calcarenite breccia enclosed in concretionary wrappings. The caliche itself is in parts vesicular and porous, in parts very dense and compact. Though no sections were available, it seemed clear that the strata had been arched up in the process of caliche formation.

The ridges form for the most part a parallel system along NW-SE lines. Air photographs show that this trend coincides with one of the two major joint directions in this area. They also reveal the extent of the ridge group to be approximately 1500 yards in length and 750 yards in width. Although the ridges are so low that they cannot be recognized with certainty on the available photographs, it seems likely that there are further groups of similar ridges in the area.

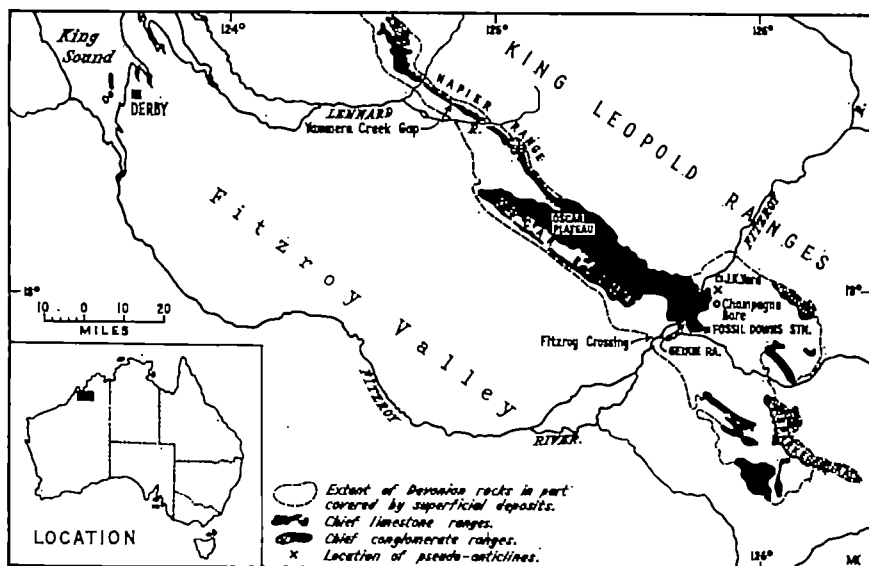


Fig. 1. Map to show location of the Limestone Ranges of the Fitzroy Basin and site of the caliche pseudo-anticlines.

In all dimensional respects the Western Australian examples tally very closely with the Mexican counterparts, but there is one important point of difference. Whereas Price regards the intercalation of weak shales as an important factor in the occurrence and distribution of these pseudo-anticlines, the Fossil Downs examples are developed entirely in competent beds and bear witness even more emphatically to the powerful forces due to volumetric changes brought into play by the pedogenic processes.

Price took the view that the phenomena he observed were actively in progress and to be related to present climatic conditions, though many of the

buckles were eroded along their axes. Not one of his three figured sections shows the surface reflecting the form of the dislocated beds. There is even more reason to regard the Fossil Downs ridges not as relict landforms produced by processes no longer operative but as actual expressions of current processes, as in all the cases observed here the pseudo-anticlines are faithfully reproduced in the surface form.

In terms of the governing climate, Price was content to refer simply to semi-arid conditions. Discussing the formation of caliche itself, Bretz and Horberg (1949) stress seasonal concentration of moderate rains of high intensity and rapid evaporation as necessary to produce the required alternation of downward solutional movement of soil water and upward capillary rise accompanied by deposition of the carbonates. In agreement with these conditions, it is to be noted that the Fitzroy Basin falls into the BSw climatic type of the Köppen 1932 system, into DAw in the Thornthwaite 1931 classification. The nearest rainfall station to the locality concerned, Fossil Downs Homestead some 11 miles away, has a mean annual rainfall of 18.38 inches in an average of 41 raindays of 0.1 inch or over. The rainfall intensity is undoubtedly high, associated with a substantial frequency of thunderstorms. The mean annual temperature is over 80°F and the average number of days which reach or exceed 100°F is about 100. Though rapid evaporation can also be due to strong winds and low relative humidity, it is probable that high temperatures are critical in the formation of caliche pseudo-anticlines. More explicitly than Price's discussion sets out, these landforms must be considered as elements not

PLATE 1



The nose of a caliche pseudo-anticline; the dip of the calcarenite on the near limb can be seen.

of all semi-arid morphodimatic systems but only of these in the warm-temperate and hot climatic zones.

Apart from their intrinsic interest, these caliche pseudo-anticlines have a wider significance in at least two respects in the Limestone Ranges.

(a) Although pseudo-anticlines were recognized only at the Fossil Downs locality described, caliche is widespread, particularly over the pediments which surround the Limestone Ranges. Large areas are mapped as covered by caliche in Guppy and others (1958), and usually these areas are occupied by systems of caliche ridges of similar dimensions to the pseudo-anticlines. Predominantly these ridges follow the strike of the Devonian rocks, very often the strike of the forereef facies, which are marked by steep depositional dips tectonically almost undisturbed (McWhae and others, 1958, p. 42). Price gave the warning that, where caliche disturbance was likely, the dips of bedrock outcrops, apparently in situ, could not be accepted at their face value.² This point has relevance here in the Fitzroy Basin. Northwest of the Yammera Creek water gap in the Napier Range and a few hundred yards southwest of the latter's western scarp, an outcrop of thin-bedded buff calcarenite had a dip of about 70° to the southwest. The forereef depositional dips in the scarp behind were only 20-30°. The possibility that at the outcrop in the pediment an original dip of this latter order has been steepened by superficial disturbance due to caliche formation must be regarded as at least as likely as that of tectonic movement.

(b) Much of the southwestern scarps of the Oscar and Napier Ranges are fronted by narrow, bare pediments, beautifully planed across the steeply dipping forereef beds. Farther out series of caliche ridges, predominantly parallel with the strike of these beds, descend gently with overall angles of 1-3°. Beyond there occur outcrops of Fairfield Beds (the uppermost Devonian member) and Laurel Beds (Carboniferous). The caliche belt could be taken to overlie these latter formations, which are less completely calcareous than the forereef beds and include marls and shales; the first caliche ridge would then be regarded as the limit of the forereef deposits. However, the Fossil Downs locality shows that caliche ridges, there of pseudo-anticline type, can develop on pure and competent limestone formations, thus weakening the case for adopting the first caliche ridge as the boundary indicator.

Understanding of the surrounding pediments is integral to the study of the karst morphology of the ranges, and therefore the recognition of the occurrence of pseudo-anticlines is significant for the geomorphological investigation as well as for the stratigraphic mapping of the area.

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² Brunnschweiler (1957, p. 8) has made this same point in respect of buckling of beds of the Broome Sandstone Formation between tidemarks on the coast of the nearby Dampier Peninsula. Here the buckling is attributed to the swelling effect of sea water imbibed by the clayey siltstones in the formation. Cf. also the surface deformation of laminated sandstones in the Delaware Basin of western Texas and New Mexico; these "tepees" structures are described by Newell and others (1953, p. 126).

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A REDETERMINATION OF EQUILIBRIUM RELATIONS BETWEEN KYANITE AND SILLIMANITE

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ABSTRACT. The equilibrium curve between kyanite and sillimanite has been established by quenching experiments at temperatures between 1000°C and 1500°C and pressures between 17 and 24 kilobars. The curve is given by the expression $P = 4.1 + 13.2 \times 10^{-4} T$, where the pressure, P , is in kilobars and the temperature, T , is in degrees Centigrade. There is some evidence that the phase boundary may depart from linearity at low temperatures, but no quantitative estimate of the amount of curvature can be obtained from present data.

If kyanite forms stably in nature, pressures of nearly 10 kilobars are required. This is equivalent to the weight of about 30 kilometers of overburden. Such great depths of burial are not required if pressure is contained by the strength as well as by the weight of the overlying rock. It is suggested that "tectonic overpressures" of a kilobar or more may exist in rocks which are undergoing deformation.

The inversion of kyanite to sillimanite is the simplest of the classical metamorphic isograds to characterize chemically. Both minerals are close to Al_2SiO_5 in composition, with other elements usually present in very small amounts. Hence they may be regarded as pure phases of the same composition, and their equilibrium relations are therefore unaffected by complicating factors such as the bulk composition of the rock in which they occur or partial pressures of volatile components. The determination of their fields of stability in the laboratory carries direct implications about the conditions under which they were formed in rocks, subject only to the assumption that chemical equilibrium is closely approached in nature.

The chemical simplicity of these phases does not imply that reactions involving them are easy to produce in the laboratory. Both are extremely refractory and react with great reluctance at temperatures below 1000°C. In earlier work on this system (Clark, Robertson, and Birch, 1957), the temperatures required for reaction to take place in a reasonable time were uncomfortably close to the maximum attainable. The number of successful runs at high temperatures was limited by failure of the apparatus, and the reversibility of the reaction was perhaps not demonstrated as convincingly as one might desire. A phase boundary, based largely but not entirely on syntheses of kyanite or sillimanite, was established between 1000°C and 1300°C, despite these difficulties.

It is comparatively easy to maintain high temperatures and pressures for extended periods of time in apparatus in which pressure is transmitted by a plastic solid and the charge is heated by a tubular graphite heating element. Such apparatus has the disadvantage that the pressure must be calculated from the force applied to the piston which produces it, and corrections for friction and the finite strength of the pressure-transmitting medium must be made. In

the previous work the pressure was measured directly and precisely by the change in resistance of a coil of manganin wire.

The present results, obtained with a solid pressure-transmitting medium, prove to be in good agreement with the previous experiments. Since the equipment used in the two studies is basically different, this agreement suggests strongly that both sets of data are essentially correct. It appears that the calculation of pressure in the present work is as accurate as could be expected, and it also appears that the phase boundary established previously is very close to the true equilibrium curve.

EXPERIMENTAL PROCEDURE AND RESULTS

The present work was done in apparatus that differs only in minor respects from that described by Boyd and England (1960). Calibration against the Bi I-Bi II transition, which takes place at 25.2 kilobars at 25°C, indicates that the pressure calculated from the load on the piston is greater than that experienced by the sample by about 13 percent at room temperature. This figure is reproducible to within a few tenths of one percent. Part of this loss of pressure is attributable to the strength of the talc sleeve which transmits the pressure. This will be lower at high temperatures, implying that a correction of less than 13 percent should be made. The pressures given below have been determined by reducing the value calculated from the load on the piston by 8 percent of the corrected pressure, in agreement with the practice of Boyd and England. The pressure calculated in this way is believed to be accurate to within 5 percent for the range of pressures through which the reaction could be followed in the present study.

Temperatures of the charges were measured with Pt-Pt 10 percent Rh thermocouples pressed against one end of the Pt capsule in which the charge was held. The thermal gradient in the furnace rarely exceeded 15°C in the length of the charge and never exceeded 20°C. No correction was made for the effect of pressure on the e.m.f. of the thermocouple.

Four materials were used as reactants in this study. Kyanite and sillimanite were synthesized from andalusite from Hill City, South Dakota and from metakaolinite prepared by firing Georgia kaolinite overnight at 600°C. The kaolinite, kindly supplied by G. C. Kennedy, contained as principal impurities 0.15 percent Na₂O and 0.30 percent TiO₂ (analysis by C. G. Engel). No analysis of the andalusite is available. Kyanite from Burnsville, North Carolina and sillimanite from Brandywine Springs, Delaware were also used in the experiments. An analysis of the kyanite has been given by Todd (1950). The sillimanite is probably very pure, judging by its lack of color and the relatively small values of its lattice parameters (Skinner, Appleman, and Clark, 1961). Fine-grained samples of the aluminosilicates were prepared by elutriating in water for 6 minutes.

Experimental results are given in table 1 and are shown in figures 1 and 2. Products were identified by their X-ray diffraction patterns. The phase boundary in figure 2 is the same as that determined by the syntheses shown in figure 1. This boundary is reversible to within a kilobar, and the results of the experiments are insensitive to the particular reactant used. This conclusion was

TABLE 1
Experimental Results

°C Temperature	Kilobars Pressure	Hours Duration	Reactants	Products
1500	23.6	3	K + (S)	S
1500	24	2	A	S
1500	24	2	A	S + Q* + C*
1500	24.5	2	A	K
1500	25	2½	S + (K)	K + (S)
1400	22	2¼	A	S
1400	22	5	K + (S)	K + (S)
1400	22	5¼	K + (S) + H ₂ O	K + C + G
1400	22	5	K + (S)	S + (K)
1400	22.5	4	A	K + S + Q* + C*
1400	23	5	S + (K) + H ₂ O	C + G
1400	23	3	A	K + Q* + C*
1400	23.1	5	S + (K)	K
1350	21	5	K + (S)	S + (K)
1300	20	4½	K + (S)	K + (S)
1300	20.5	4½	K + (S)	K + (S)
1300	20.5	2¼	MK	S + Q
1300	21	2	MK	S + K + Q
1300	21.5	2	MK	K + Q
1300	22	5	S + (K)	K
1200	19.5	3	MK	S + Q + C*
1200	20	2¾	MK	K + S + Q + C*
1200	20.5	2¾	MK	K + Q
1100	18	4½	MK	S + Q + C*
1100	18.5	5	MK	S + (K) + Q + C*
1100	19	4	MK	K + Q
1000	17	6½	MK	S + Q + C*
1000	17.5	6¾	MK	S + Q + C*
1000	18	5¼	MK	K + Q + C*
900	15	18	MK + (K) + (S)	S + (K)
900	15.5	16¾	MK + (K) + (S)	S + K
900	16.5	15	MK + (K) + (S)	K + S
900	17	15	MK + (K) + (S)	K + (S)

MK, metakaolinite; A, andalusite; K, kyanite; S, sillimanite; G, glass; Q, quartz; C, corundum.

Parentheses indicate phase present in minor amounts. *Metastable phase.

arrived at previously (Clark, Robertson, and Birch, 1957), but the present evidence is much less equivocal.

Kyanite and sillimanite were synthesized together in several runs close to the equilibrium curve. This is probably due to small gradients of pressure and temperature. The persistence of both phases can be attributed, in part at least, to the extreme sluggishness with which reaction between kyanite and sillimanite takes place close to the equilibrium curve.

Attempts were made to locate the equilibrium curve at temperatures below 1000°C, using as a reactant metakaolinite seeded with about 10 percent each of kyanite and sillimanite. In runs 1 kilobar or more away from the extrapolated phase boundary at 900°C, the polymorph stable under the conditions of the experiment was decidedly the more plentiful product of the run. The results of runs closer to the equilibrium curve were not sufficiently clearcut

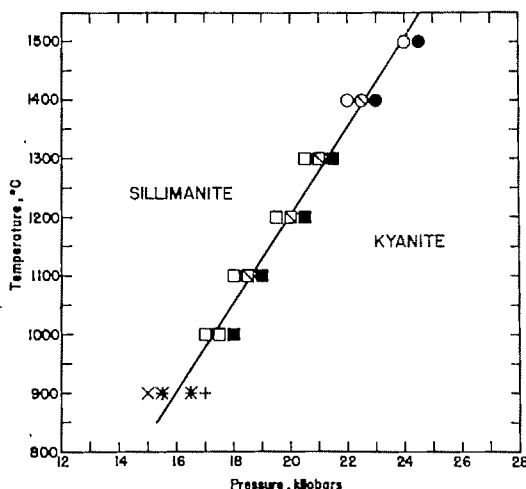


Fig. 1. Syntheses of kyanite and sillimanite. Circles stand for runs in which andalusite was the reactant, squares represent metakaolinite, and crosses and pluses represent metakaolinite seeded with kyanite and sillimanite. Solid symbols mean kyanite was produced, open symbols mean sillimanite, and open symbols with a diagonal line mean both. Crosses represent the growth of sillimanite and pluses the growth of kyanite.

to permit them to be assigned definitely to either field of stability. Both kyanite and sillimanite grew in about equal amounts.

Several experiments in which the reactant was either kaolinite or an aluminosilicate to which a small amount of water had been added were carried out at temperatures above 1000°C. These runs produced corundum plus glass, in agreement with the results of Yoder and Schreyer (1959) at lower pressures. The water content of these charges is not really known, as it was not possible to demonstrate the absence of leak during the run. These observations of melting are of only qualitative value as a result. The appearance of corundum in these experiments is of interest because it suggests a possible explanation of the metastable formation of quartz plus corundum that plagued the previous study (Clark, Robertson, and Birch, 1957). In those runs, kaolinite or andalusite which contained pyrophyllite as an impurity were heated in unsealed capsules. It is possible that partial fusion and the nucleation of corundum took place before all the water escaped. Once formed, corundum will persist practically indefinitely. The appearance of this metastable assemblage was not troublesome in the present work.

COMPARISONS WITH OTHER WORK

The present results are compared with those of the previous study (Clark, Robertson, and Birch, 1957) in figure 3. Within the common range of experiment (1000°C to 1300°C) the two sets of data agree to within 1 kilobar. The discrepancy could be reduced by applying a smaller correction for friction and the strength of the pressure medium to the present results, but the difference is probably within experimental error as it stands. It may also be a measure of the width of the zone of indifference between kyanite and sillimanite.

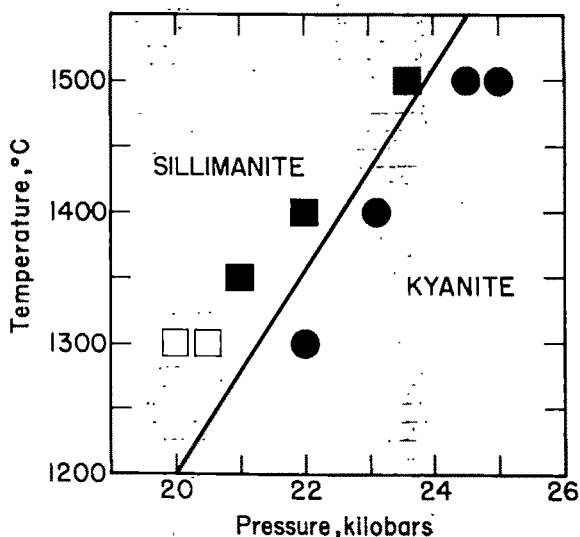


Fig. 2. Conditions under which the reaction was reversed. Solid squares represent sillimanite formed from kyanite, solid circles represent kyanite formed from sillimanite, and open squares represent unaffected kyanite.

The curves in figure 3 have been extrapolated to low temperatures without regard for other reactions that complicate the stable phase diagram. Natural occurrences suggest the existence of a triple-point between andalusite, kyanite, and sillimanite at moderate temperatures and pressures. It has also been suggested, although not demonstrated, that quartz plus corundum have a field of stability (Aramaki and Roy, 1958). This suggestion does not agree well with natural evidence; in the rare cases in which they both occur in the same rock, quartz and corundum are usually separated from each other by an aluminous silicate. One of the commonest occurrences of margarite is as a coating surrounding corundum crystals in quartzose rocks (Pratt and Lewis, 1905).

The slope of the phase boundary determined in the present study is 13.2 bars/degree. This is slightly larger than the value found previously (about 10 bars/degree), but it is decidedly smaller than the slope calculated from room-temperature thermochemical data. Todd (1950) found that the change in entropy of the reaction at room temperature was 123 ± 6 decijoules/mol°C, and an extensive study of the lattice parameters of kyanite and sillimanite (Skinner, Clark, and Appleman, 1961) shows that the change in volume is 5.80 ± 0.03 cm³/mol. According to these figures, the slope of the phase boundary is 21.2 ± 1.1 bars/degree.

High-temperature X-ray studies at atmospheric pressure (Skinner, Clark, and Appleman, 1961) show that kyanite has a larger thermal expansion than sillimanite at moderate temperatures. $(\partial \Delta V / \partial T)_{P=0}$ is about 0.4×10^{-3} cm³/mole °C at 200°C and decreases at higher temperatures. The net decrease in ΔV between 0° and 1000°C is about 3½ percent. It is unlikely that this result will be greatly altered at the pressures of the equilibrium curve. The effect of pressure on ΔV is likely to be no larger than the effect of temperature

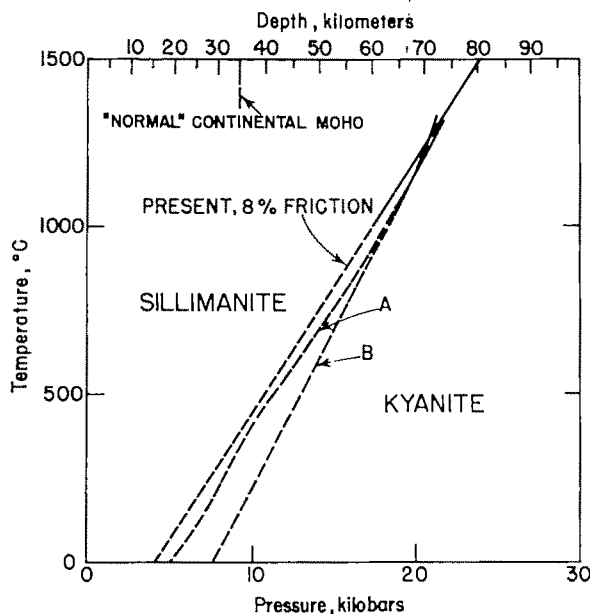


Fig. 3. Comparison with previous work. Curves *A* and *B* are the curves given by Clark, Robertson, and Birch (1957, fig. 2).

according to the argument given previously (Clark, Robertson, and Birch, 1957).

The effect of pressure on ΔS , the entropy change of the reaction, is given by the Maxwell relation $(\partial \Delta S / \partial P)_T = -(\partial \Delta V / \partial T)_P$. At high temperatures the pressure effect is small because $(\partial \Delta V / \partial T)_P$ is small, and at low temperatures it is small because the pressures of the equilibrium curve are low. The increase in ΔS is unlikely to exceed 3 percent under any conditions. The effect of allowing for the derivatives of volume and entropy discussed so far is to increase the slope of the phase boundary, in conflict with the experimental results. But the predicted increase is much less than the reduction in slope of about 50 percent that is required to secure agreement between the high-temperature, high-pressure experimental results and the room-temperature thermochemical data.

Measurements of heat capacity at high temperatures (Kelley, 1949) indicate that a change in ΔS with temperature may alter the slope of the phase boundary by roughly the amount required to bring the two sets of data into agreement. The change in slope may be uncertain by as much as 50 percent, however, and no account was taken of the correction in drawing the phase boundary in figure 3 for this reason. Because heat capacities of solids usually depart most widely from their classical values at low temperatures, most of the curvature probably takes place below 500°C. Hence the position of the phase boundary will not be greatly affected by this correction.

GEOLOGICAL IMPLICATIONS

The high pressures required to form kyanite stably, which were an unexpected result of the previous work (Clark, Robertson, and Birch, 1957), are substantiated by the present study. Temperatures of a few hundred degrees seem to be required to produce regional metamorphism, which means that a pressure of 7 to 10 kilobars is roughly the minimum compatible with stable formation of kyanite in nature.

Depths of burial are commonly related to pressure by $P = \bar{\rho} gh$, where $\bar{\rho}$ is the mean density between the surface and depth h , and g is the gravitational acceleration. The scale at the top of figure 3 has been calculated for $\bar{\rho}$ equal to 2.67 gm/cm³ in the crust and 3.33 gm/cm³ in the mantle. A depth of more than 35 km is required to reach a pressure of 10 kilobars; this implies that kyanite schists formed at depths equivalent to those towards the base of the "normal" sea-level crust, on this model. This conclusion does not follow if the phase boundary has appreciable curvature at high temperatures, but such behavior, although not impossible, is certainly improbable.

If kyanite-bearing rocks are to be formed at depths in excess of 20 km, large vertical movements must have taken place in the past. Such large amplitudes of motion might accompany the formation of a major mountain root, but they seem unlikely to result from less extreme orogenic episodes. The depth required for the stable formation of kyanite in a mountain root may be greater than that required elsewhere because of the high temperatures that may exist in a thickened crust (Birch, 1950; Clark and Niblett, 1956). This could lead to the formation of zones of kyanite-bearing rocks near the margins of the root, with sillimanite in the central, hot portion. This is the spatial distribution of the aluminosilicates found in New Hampshire, for example (Billings, 1956).

These great depths of burial can be escaped, or at least lessened, if pressures in the crust are sustained by the strength as well as the weight of the overlying rock. The mere existence of deformation in metamorphic terrains implies that stress differences exceeded the strength of the rocks, and the nature of the deformation suggests that the stresses causing it were compressive relative to $\bar{\rho} gh$ rather than tensile. This implies that the mean of the principal stresses at times exceeds $\bar{\rho} gh$. The magnitude of this "tectonic overpressure" is set by the strength of the rocks that support it.

A rough notion of how large the overpressure may become may be obtained from a simple model. Consider a small spherical cavity in the Earth inside which the pressure is P , and suppose that the stress due to the weight of the overlying rock is simply a hydrostatic pressure. In this case the stress difference in the rock surrounding the cavity is zero when $P = \bar{\rho} gh$. We now calculate the largest value of $P_{\#} = P - \bar{\rho} gh$ allowed by the strength of the wall rock. $P_{\#}$ can be identified with the maximum tectonic overpressure in that it is the maximum mean stress that can be contained. No account of the origin of this pressure is given. It is assumed that tectonic forces do in fact build up the maximum tolerable pressures, and that they are relieved by yielding of the rocks, probably mainly in the vertical direction.

If the wall rock behaves as a perfectly plastic material obeying the Tresca yield criterion (which in this case states that the maximum stress difference cannot exceed Y , the yield point in simple tension), the maximum permissible value of P_H is (Hill, 1950, p. 104):

$$P_H = 2/3 Y \ln (E/3(1-\sigma)Y).$$

If Poisson's ratio, σ , is set equal to $1/3$, and Young's modulus, E , is taken to be 500 kilobars (Birch, Schairer, and Spicer, 1942), P_H is found to be 3.7 kilobars if $Y = 1$ kilobar and 0.52 kilobars if $Y = 0.1$ kilobar. If plastic flow is not allowed in the wall rock, $P_H = 2/3 Y$, a result which is identical to that obtained by Birch (1955) from a different argument.

Griggs, Turner, and Heard (1960) have observed tensile strengths greater than 1 kilobar in several rocks at 5 kilobars confining pressure and 800°C . As these authors are careful to point out, however, the experimental results refer to rates of strain that may exceed those occurring in nature by a factor as large as 10^{12} . This implies that the strengths of rocks may be substantially smaller under natural conditions than under the conditions of these laboratory tests. This problem is complicated by recrystallization. The strength of a rock under natural conditions may be determined by the relative rates of deformation and recrystallization.

An overpressure persisting for only a few thousand years, a time that is short geologically speaking, could significantly affect the mineralogy of the rock. A value of Y of a few hundred bars might persist for short times during active deformation; this leads to overpressures of 1 kilobar or more. Since 1 kilobar corresponds to the weight of nearly 4 km of overburden in the crust, the reduction in the depth of burial required may be considerable.

Evidence of the existence of tectonic overpressures in rocks, other than the fact that deformation takes place, is usually indefinite. No clearcut distinction between tectonic pressure and deep burial can be made in most regionally metamorphosed terrains, because no way of determining depth independently of pressure has been found. Estimates based on thickness of strata are vitiated by tectonic thickenings and thinings of unknown magnitude. Although distorted crystals of kyanite are common, they only show that deformation followed growth. It may also have accompanied it, but there is no proof of this. An unusual local occurrence of kyanite is in the contact aureoles of granitic bodies in SW Ankole. Combe (1932) noted that kyanite occurs in the schists only where they have been strongly deformed by the forceful emplacement of the granites.

The hypothesis of tectonic overpressures represents a return to the stress mineral concept of Harker but in modified form. Harker supposed that the fields of stability of minerals were influenced by shear. This idea has fallen into disrepute in recent years, both on theoretical grounds (Verhoogen, 1951; Macdonald, 1957) and because of the occurrence of stress minerals in rocks that show little or no evidence of deformation (Miyashiro, 1949, 1951). Tectonic overpressures provide a different reason for "stress minerals" (most of which are in reality high-pressure minerals) to be associated with shear. In the present view, shearing stresses make possible an increased mean principal

stress and bring high-pressure minerals into their fields of stability at depths where they would normally be unstable at the prevailing temperature.

The real basis of the stress mineral concept is petrographic observation, although Harker (1939) also cited the experimental evidence then available in its support. The concept is not the result of any single observation, but rather the result of accumulated experience that certain minerals, one of which is kyanite, characteristically occur in strongly deformed rocks. Although Harker's explanation of it is probably wrong, the association of kyanite with deformation nonetheless exists. An attractive feature of the hypothesis of tectonic overpressures is that it provides a natural explanation of some of the observations that formed the basis of the stress mineral concept.

It cannot, of course, be inferred that all kyanite is produced in regions of tectonic overpressure. Considerable depths of burial are undoubtedly necessary as well. It is highly desirable that the rough calculations used here to arrive at an upper limit to the tectonic overpressure be refined and improved as experimental data on the strength of rocks accumulated. A better understanding of the stresses and movements that have affected the Earth's crust can emerge from such work, and this is almost certain to advance our knowledge of orogenic and metamorphic processes.

ACKNOWLEDGMENTS

I am indebted to T. N. Clifford for calling my attention to the kyanites of Ankole and to G. A. Chinner for reading the manuscript and making numerous suggestions which led to its improvement.

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MOLAR VOLUMES AND THERMAL EXPANSIONS OF ANDALUSITE, KYANITE, AND SILLIMANITE*

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and DANIEL E. APPLEMAN**

ABSTRACT. Precise measurements of unit-cell parameters of four andalusites, four sillimanites, and five kyanites from different localities lead to the following molar volumes at 25° C:

Andalusite	51.550 ± 0.011 cm ³ /mol
Sillimanite	49.918 ± 0.015 cm ³ /mol
Kyanite	44.116 ± 0.021 cm ³ /mol

Unit-cell parameters at high temperatures were measured with a heating stage on an X-ray diffractometer. From these data the molar volumes and thermal expansions of all three minerals were obtained between 25°C and 1050°C.

INTRODUCTION

Molar volume is one of the most important parameters involved in calculations of phase equilibria from thermodynamic data. Ideally, an equation of state defining the molar volume over a wide range of temperatures and pressures is desirable. For many minerals, however, even the molar volume at room temperature and pressure is not accurately known, and volume changes with changing temperature have been little studied.

The present work was undertaken with two principal aims in mind. We sought first to measure with high precision the unit-cell parameters of andalusite, kyanite, and sillimanite at room temperature in order to calculate the molar volumes at 25°C and one atmosphere. The differences in molar volume among the three polymorphs at 25°C, which are needed in the calculations of the slopes of the equilibrium curves from Clapeyron's equation, are easily derived from these data.

Our second aim was to obtain accurate measurements of the unit-cell parameters of each mineral at high temperatures. From these data the effect of temperature on the differences in molar volume between the aluminosilicates can be obtained, and the values of the coefficients of thermal expansion can also be found.

In the cases of andalusite and sillimanite, which are orthorhombic throughout the temperature range of investigation, symmetry requires that the principal axes of linear thermal expansion coincide with the crystallographic axes. The magnitude of the thermal expansion in the principal directions is given simply by the changes in length of the three edges of the unit-cells, which were the quantities measured at high temperatures. Kyanite is triclinic, however, and there are no symmetry requirements controlling the orientation of the principal axes of linear thermal expansion relative to the crystallographic axes. Our high-temperature measurements on kyanite are not precise enough to permit accurate calculation of both the lengths and orientations of the principal axes of expansion because of accumulation of experimental error. For all three minerals most emphasis has been placed on the volume expansion.

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sion, since this is the most important quantity for theoretical purposes, and since it can be calculated without knowledge of the orientation of the principal axes.

MOLAR VOLUMES AT ROOM TEMPERATURE

Since we are interested in the molar volumes of the minerals as they occur in nature, two sources of uncertainty must be recognized. Our results are affected both by errors of measurement and by real differences between material from different localities. In order to investigate the possible range of unit-cell parameters in nature, measurements were made on specimens of each mineral from several different localities. Both the errors of measurements and the natural variability of these minerals appear to be small, and we believe that the molar volume of any given specimen will lie within 0.1 percent of our mean values, unless a very impure sample has been selected.

It would be desirable, of course, to supplement this work with measurements on pure synthetic material. This has not been possible because the available synthetic phases are too fine grained and too imperfectly crystallized to allow accurate unit-cell measurements.

As the molar volumes were calculated from the dimensions of the unit-cells, accurate knowledge of the molar volumes depends on the accuracy of the X-ray measurements, most of which were made on a focusing diffractometer. X-ray powder films taken using the Wilson (1949) technique proved helpful in resolving weak lines for indexing the diffraction patterns. The parameters of the unit-cell of kyanite were also checked by precise precession photographs. Molar volumes were calculated using $6.02472 \times 10^{23} \text{ mol}^{-1}$ for Avogadro's number (DuMond and Cohen, 1953). Molar volumes derived in this way are gram-formula volumes on the physical scale of atomic weights.

Sillimanite proved to be the most easily handled polymorph. Indexed powder data are given in table 1, and the unit-cell dimensions are given in table 2. These dimensions were calculated independently from measurements of the (520), (250), and (004) reflections and from (420), (240), and (002). The 2θ angles were determined by scanning the sillimanite reflections and those of an internal standard from three to five times in each direction. NaCl ($a = 5.64028 \text{ \AA}$, Frondel, 1955) was the internal standard for the (002) reflection, and CaF_2 ($a = 5.4628$) was the internal standard for all the others. The cell dimension of the CaF_2 used in this work was determined by comparison with the NaCl standard. Hence all our results are affected equally by any errors in the cell dimensions of the internal standards.

The cell dimensions of sillimanite were determined by averaging the data obtained from the (520), (250), and (004) reflections with those found from (420), (240), and (002), after weighting the results in inverse proportion to their standard deviations. The difference between the two sets of data never exceeded one part in 1500 and usually was much less than this. The average is thought to have an accuracy of at least one part in 5000, judging from the internal consistency of the data.

Results for material from four localities are given in table 2. They fall into two groups which appear to reflect slight differences in composition. The specimen from Willimantic, Connecticut was chocolate-brown, suggesting that

TABLE 1

Sillimanite, Williamstown, South Australia

Indexed powder diffraction measurements for sillimanite from Williams-town, South Australia, (USNM. R10532). Intensity (I) visually estimated from powder film. All permissible hkl in space group $Pbnm$ calculated from cell having $a = 7.4817 \text{ \AA}$, $b = 7.6712 \text{ \AA}$, $c = 5.7693 \text{ \AA}$.

<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>	<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>
3	110	5.363	5.356		142		1.562
1	101	4.575	4.569	0.5	223	1.5625	1.562
	111		3.925	1	412	1.5385	1.538
0.5	020	3.839	3.836		303		1.523
1	200	3.751	3.741	5	340	1.5200	1.520
10	120	3.413	3.413		332		1.518
10	210	3.365	3.363		430		1.510
	021		3.194		133		1.506
	121		2.938		150		1.503
	211		2.905		313		1.494
3	022	2.888	2.885		341		1.470
4	220	2.688	2.678		510		1.469
5	112	2.541	2.540		242		1.469
2	221	2.428	2.429		431		1.461
	130		2.420	0.5	151	1.4559	1.455
	310		2.372	1	422	1.4537	1.453
0.5	022	2.3055	2.305		501		1.449
2	301	2.2890	2.289	2	004	1.4423	1.442
	202		2.284		511		1.423
0.5	131	2.2317	2.231		233		1.422
7	122	2.2026	2.203	1	250	1.4205	1.420
	311		2.194		323		1.415
	212		2.189	1	520	1.3947	1.394
4	230	2.1115	2.111		114		1.393
0.5	320	2.0914	2.091	1	251	1.3780	1.378
1	231	1.9832	1.983		043		1.358
	321		1.966		521		1.355
	222		1.963		024		1.350
0.5	040	1.9181	1.918		204		1.346
1	400	1.8712	1.871	0.5	342	1.3441	1.345
	103		1.863	1	440	1.3391	1.339
	140		1.858		432		1.338
	132		1.854		143		1.336
1	312	1.8332	1.832	1	152	1.3327	1.333
1	041	1.8197	1.820		124		1.329
	410		1.817	1	214	1.3267	1.326
	113		1.810		413		1.321
0.5	330	1.7856	1.785	1	512	1.3101	1.309
	141		1.768		333		1.308
	411		1.733		350		1.307
	023		1.719		441		1.304
2	240	1.7081	1.707	0.5	530	1.2917	1.292
	331		1.706		060		1.279
	232		1.704		243		1.277
0.5	322	1.6936	1.693	3	351	1.2757	1.275
2	420	1.6811	1.681		252		1.274
	123		1.675		224		1.270
	213		1.669		423		1.266
	421		1.614	2	160		1.260
3	042	1.5966	1.597		531	1.2590	1.260
1	402	1.5700	1.569		522		1.255

TABLE 2
Unit-cell edges of sillimanite, 25°C

	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>V</i> , Å ³	<i>V</i> , cm ³ /mol
Brandywine Springs, Delaware USNM. 79748	7.4806 ± .002	7.6709 ± .002	5.7678 ± .002	330.97	49.850
Benson Mines, New York	7.4861 ± .002	7.6750 ± .002	5.7747 ± .002	331.79	49.974
Willimantic, Connecticut USNM. C3019	7.4843 ± .002	7.6751 ± .002	5.7730 ± .002	331.62	49.948
Williamstown, South Australia USNM. R10532	7.4817 ± .002	7.6712 ± .002	5.7693 ± .002	331.12	49.873
Mt. Crawford* South Australia	7.4864	7.6727	5.7716	331.52	49.933
Connecticut*	7.4839	7.6758	5.7728	331.62	49.948
Sterling Hill,* New Jersey	7.4876	7.6718	5.7704	331.46	49.924
Finkenbergl, Germany*	7.4839	7.6718	5.7692	331.24	49.891

* Agrell and Smith (1960)

Mean volume = 49.918 ± 0.015 cm³/mol

Range = 49.850-49.974

Standard deviation = 0.041 cm³/mol

it contains a considerable amount of iron in solid solution. The material from the Benson Mines, New York, contains nearly 1 percent Fe₂O₃ according to the analysis given by Todd (1950) (see table 3), and it occurs with magnetite and hematite. The other sillimanites are probably closer to pure Al₂SiO₅ in composition, and their cell dimensions are smaller.

Agrell and Smith (1960) have published precise cell constants of sillimanites from four localities. Their results are also given in table 2. The mean value of the molar volume calculated from their data is 49.924 cm³/mol, in good agreement with the value of 49.911 cm³/mol calculated from ours. The difference, less than 0.03 percent, is well within our estimated uncertainty.

Agrell and Smith's sample from South Australia is from a locality that is closely adjacent to, or perhaps identical with, the locality of one of our samples. Our measurements of the South Australian sillimanite lead to smaller cell dimensions than those given by Agrell and Smith, but only in the case of the *a*-axis is the difference large (4 parts in 7000). Agrell and Smith claim an accuracy of one part in 7000 for the *a* and *b* axes, but an occasional discrepancy as large as that observed is probably not surprising. There is of course no guarantee that the compositions of the two specimens are identical.

Investigation of andalusite proved to be more difficult than that of sillimanite because the andalusite powder pattern is characterized by numerous

TABLE 3

Published analyses of materials used in this study.
Splits of the analyzed materials were used in this work.

	Andalusite* Laws, California	Andalusite** Standish, Maine	Kyanite** Burnsville, North Carolina	Sillimanite** Benson Mines, New York
SiO ₂	34.92	36.84	36.90	36.44
TiO ₂	0.63	trace	none	none
Al ₂ O ₃	59.61	63.15	63.20	61.80
Fe ₂ O ₃	0.66	0.11	0.10	0.98
FeO	—	none	none	0.14
MgO	none	trace	none	0.24
MnO	none	trace	none	0.04
CaO	0.28	0.02	0.05	0.07
Na ₂ O	0.10	none	none	trace
K ₂ O	0.13	none	none	none
P ₂ O ₅	—	—	—	0.28
H ₂ O	3.71	—	—	—
F				0.04
Total	100.04	100.12	100.25	100.03

* Clark et al., (1957)

** Todd (1950)

Trace means <0.01 percent.

nearly coincident reflections. This increased the difficulty in indexing the pattern, and it made some of the strong reflections unsuitable for the determination of unit-cell dimensions. Accurate parameters from precision Weissenberg photographs, supplied by M. J. Buerger and C. W. Burnham (personal communication, 1960) aided in the indexing. The indexed powder data are given in table 4.

The cell dimensions of andalusite, given in table 5, are remarkably uniform with the exception of the sample of viridine. This is true despite differences in color between the various samples. The andalusites from Standish, Maine, and from Hill City, South Dakota, are flesh-pink in color, but the materials from California and Brazil are greenish. An analysis of the andalusite from Standish is given by Todd (1950) and an analysis of bulk material from Laws, California is given by Clark, Robertson, and Birch (1957). These analyses are repeated in table 3. The latter sample contained minor pyrophyllite and sphene as accessories.

The lengths of the *c*-axes were calculated from the (002) and (004) reflections using CaF₂ as an internal standard. These reflections are close to (220) and (440) respectively, but by scanning slowly (1/8 degree per minute) with 0.003-in. receiving slits the doublets were easily resolved. The *a* and *b* dimensions were found from the (301) and (031) reflections (which are free from interference by other lines) using NaCl as an internal standard.

The viridine specimen was included in this study as an indication of the effect on the cell dimensions of extensive substitution of trivalent manganese

TABLE 4

Andalusite, Minas Gerais, Brazil

Indexed powder diffraction measurements for andalusite from Minas Gerais, Brazil (USNM R3717). Intensity (I) visually estimated from powder film. All permissible hkl in space group $Pnnm$ calculated for a cell having $a = 7.7950\text{\AA}$, $b = 7.8996\text{\AA}$, $c = 5.5580\text{\AA}$.

<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>	<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>
10	110	5.542	5.549	2	411	1.7909	1.791
	011		4.546		240		1.762
9	101	4.527	4.526	1	113	1.7573	1.757
	020		3.950	3	331	1.7543	1.755
7	111	3.924	3.927		420		1.748
	200		3.898	1	232	1.7157	1.716
6	120	3.524	3.524		322		1.711
4	210	3.490	3.495	1	241	1.6808	1.679
	121		2.976	0.5	421	1.6666	1.667
	211		2.959		123		1.640
2	002	2.780	2.779	1	213	1.6351	1.637
9	220	2.773	2.774	0.5	042	1.6100	1.610
	130		2.495	3	402	1.5950	1.596
2	112	2.4863	2.485		142		1.577
2	221	2.4819	2.482		340		1.572
5	310	2.4666	2.468		430		1.567
2	031	2.3778	2.380		412		1.564
2	301	2.3531	2.354	1	150	1.5480	1.549
	131		2.276	3	223	1.5416	1.541
4	022	2.2726	2.273		332		1.540
	202		2.263	1	510	1.5300	1.530
4	311	2.2551	2.256		051		1.520
1	230		2.182		033		1.515
1	122	2.1809	2.182	1	341	1.5126	1.513
	212		2.175	1	303	1.5088	1.509
9	320	2.1702	2.171		431		1.508
1	231	2.0315	2.031	1	501	1.5013	1.501
	321		2.022		151		1.492
2	040	1.9753	1.975	4	242	1.4881	1.488
	222		1.963		133		1.487
1	400	1.9475	1.949	2	313	1.4826	1.482
1	140	1.9145	1.915		422		1.479
2	410	1.8921	1.892	2	511	1.4759	1.475
2	132	1.8564	1.856	2	250	1.4640	1.464
1	330	1.8509	1.850	0.5	520	1.4494	1.450
	312		1.846		251		1.416
2	141	1.8112	1.810		233		1.412
2	013	1.8045	1.804		323		1.409
	103		1.802		521		1.403
				2	004	1.3895	1.390

TABLE 4 (Continued)

<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>	<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>
2	440	1.3880	1.387		423		1.271
	342		1.369		161		1.264
	432		1.365		611		1.249
	152		1.353	1	260	1.2465	1.247
1	350	1.3497	1.350		224		1.242
	114		1.348	3	442	1.2412	1.241
	441		1.346	1	620	1.2339	1.234
	530		1.342		450		1.227
1	512	1.3390	1.340		540		1.224
0.5	143	1.3321	1.331		261		1.217
	413		1.324	1	352	1.2136	1.214
	060		1.317		134		1.214
	351		1.312		314		1.211
	024		1.311		532		1.208
	333		1.309		621		1.205
	204		1.309		053		1.202
1	531	1.3042	1.304		343		1.199
0.5	600	1.2986	1.299		451		1.198
	160		1.298		433		1.196
1	252	1.2950	1.295	1	541	1.1954	1.195
	124		1.293		503		1.193
	214		1.291		062		1.190
2	522	1.2848	1.286	1	153	1.1882	1.188
0.5	610	1.2820	1.282	2	513	1.1796	1.180
	243		1.277		602		1.177
					162		1.176

TABLE 5
Unit-cell edges of andalusites, 25°C

	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>V</i> , Å ³	<i>V</i> , cm ³ /mol
Minas Gerais, Brazil					
USNM R.3717	7.7950 ± 0.001	7.8996 ± 0.001	5.5580 ± 0.001	342.25	51.549
Standish, Maine	7.7955 ± 0.001	7.8968 ± 0.001	5.5585 ± 0.001	342.18	51.538
Laws, California	7.8012 ± 0.001	7.8998 ± 0.001	5.5570 ± 0.001	342.47	51.582
Hill City, South Dakota	7.7940 ± 0.001	7.8968 ± 0.001	5.5588 ± 0.001	342.13	51.531
Brazil*	7.7942 ± 0.0002	7.8985 ± 0.0002	5.5590 ± 0.002	342.23	51.546
Hidaka, Japan (Viridine)	7.881 ± 0.01	7.981 ± 0.01	5.614 ± 0.008	353.1	53.18

* M. J. Buerger and C. W. Burnham (personal communication, 1960)

Mean volume (excluding viridine) = 51.550 ± 0.011 cm³/mol

Range 51.531-51.582 (excluding viridine)

Standard Deviation (excluding viridine) = 0.022 cm³/mol

for aluminum. It was supplied by Yoshio Suzuki of the Geophysical Laboratory. Because of the diffuseness of the reflections and strong fluorescence of manganese in copper radiation, no attempt was made to obtain very accurate data, but it is clear that there is a very large difference between this material and the manganese-free andalusites. The molar volume of viridine is larger by about three percent. The composition of the viridine cannot be given because it is peppered with inclusions of hematite, and all attempts at separation have failed. Heinrich and Corey (1959) consider that viridine may contain up to 10 percent transition-metal oxides; this clearly influences its thermodynamic properties and probably its field of stability.

Muller-Hesse and Schwiete (1960) reported lattice parameters of andalusite. Their values of a and b are smaller than ours by about 0.1 percent, and their value of c is smaller than ours by about 0.4 percent. They give no indication of the composition or source of their material.

The indexed powder data for kyanite are given in table 6 and the unit-cell parameters of six specimens are given in table 7. Five of the samples were either colorless or pale blue. The material from Barkhamstead, Connecticut is bright green, however, and its molar volume is considerably larger than those of the other specimens. X-ray fluorescence analysis shows it to contain more than 1 percent iron and between 0.1 and 0.5 percent manganese. Most kyanites are much purer than this (Dana, 1884; Henriques, 1957). An analysis of the kyanite from Burnsville, North Carolina has been given by Todd (1950) (table 3); it is very pure.

The unit-cell parameters of kyanite were calculated from the d spacings of the (121), ($\bar{2}\bar{1}1$), (130), (140), (311), and (500) reflections, measured relative to NaCl as an internal standard. Computations were made on a digital computer, using an iterative method. The results were checked in two cases by quartz-calibrated precession photographs (table 7).

It was feared that the results of calculating six unit-cell parameters from only six measured d spacings would be affected by accumulation of random experimental errors, but the consistency of the data given in table 7 suggests strongly that this is not the case. The total range of the parameters a , β , and γ is twice our estimated uncertainty or less, and the range of b and α is within three times the uncertainty. The parameter c shows a considerably greater range than the others, but we believe that this variation reflects real differences between different samples. It may be due to a small amount of aluminum substituting for silicon in the chains which parallel the c axis in the kyanite structure.

The powder data agree well with the single-crystal data for the parameters a , b , α , β , and γ . For the kyanite from Burnsville, North Carolina, however, the data for the c parameter are in poor agreement. It should be noted that the c parameter measurements are the least precise of the single-crystal data.

The mean value of the molar volume of kyanite was computed from the powder data alone, partly for the sake of consistency and partly because these data appear to be at least as accurate as the single-crystal measurements. The green specimen from Connecticut was excluded from the average because of its high content of transition metals.

TABLE 6

Kyanite, Burnsville, North Carolina

Indexed powder diffraction measurements for kyanite from Burnsville, North Carolina. Intensity (I) visually estimated from powder film. All permissible hkl in space group PI calculated from cell having $a = 7.121 \text{ \AA}$, $b = 7.846 \text{ \AA}$, $c = 5.577 \text{ \AA}$, $\alpha = 89^\circ 58'$, $\beta = 101^\circ 09'$, $\gamma = 106^\circ 00'$.

<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>	<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>
	010		7.530				
2	100	6.698	6.706	1	{ 121	2.459	{ 2.462
1	110	5.898	5.897		{ 221		{ 2.462
	001		5.463		131		2.369
	101		4.726	4	102		2.369
	011		4.544		202	2.364	2.363
1	110	4.428	4.428		112		2.362
	011		4.309	4	212	2.357	2.358
2	111	4.304	4.304		230		2.351
	101		3.871	1	131	2.333	2.332
2	{ 111	{ 3.766	{ 3.766		031		2.331
	{ 020	{ 3.765	{ 3.765	2	310	2.329	2.329
	{ 120	{ 3.765	{ 3.765		211		2.312
	{ 111	{ 3.758	{ 3.758		311		2.308
1	210	3.443	3.443	2	{ 122	2.273	{ 2.274
10	200	3.355	3.353		{ 022		{ 2.272
	111		3.191	2	300	2.235	2.235
9	121	3.186	3.186	2	031	2.234	2.234
	211		3.184		231		2.233
	021		3.184	1	301	2.232	2.232
	201		3.154	4	{ 220	2.213	{ 2.214
3	{ 021	{ 3.022	{ 3.022		{ 320		{ 2.214
	{ 121	{ 3.021	{ 3.021	1	{ 321	2.182	{ 2.182
4	{ 120	{ 2.949	{ 2.949		{ 221		{ 2.182
	{ 220	{ 2.948	{ 2.948		112		2.170
1	210	2.784	2.786		212		2.164
	221		2.752	3	130	2.160	2.160
	121		2.751		022		2.155
	002		2.732		122		2.153
0.5	102	2.725	2.729		222		2.152
	211		2.701		122		2.150
5	211	2.696	2.695		231		2.093
	201		2.631		131		2.091
	112		2.615	2	311	2.008	2.007
	012		2.615		311		2.004
1	130	2.604	2.603		310		1.995
	012		2.523		212		1.973
5	112	2.518	2.519		312		1.969
4	030	2.510	2.510		330		1.966
				6	140	1.961	1.961

TABLE 6 (Continued)

<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>	<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>
0.5	{ 221	1.942	{ 1.943		401		1.701
	{ 321		{ 1.943		140		1.693
	301		1.937		340		1.693
6	{ 202	1.935	{ 1.936		113		1.678
	{ 131		{ 1.935		123		1.677
	331		1.933		400		1.676
3	302	1.930	1.930	2	{ 023	1.676	{ 1.676
	132		1.904		{ 213		{ 1.675
	032		1.902		103		1.674
1	{ 040	1.883	{ 1.883		341		1.666
	{ 240		{ 1.883		141		1.665
	222		1.883	1	{ 223	1.648	{ 1.651
	322		1.880		{ 123		{ 1.650
	222		1.879		231		1.626
	232		1.866		431		1.625
	132		1.866		312		1.625
	103		1.854	3	412	1.621	1.621
1	{ 141	1.845	{ 1.847		430		1.620
	{ 141		{ 1.846		132		1.608
	003		1.821		232		1.605
	241		1.812		023		1.605
	041		1.811		123		1.604
	113		1.809		222		1.596
	032		1.799		322		1.595
	132		1.796		142		1.594
	013		1.793		113		1.594
	113		1.792		242		1.593
	212		1.790		142		1.593
	312		1.785	4	{ 422	1.592	{ 1.592
	230		1.783		{ 322		{ 1.592
	331		1.776		{ 042		{ 1.592
	231		1.774		313		1.590
4	311	1.767	1.767		302		1.581
1	411	1.763	1.764		402		1.577
	203		1.755		303		1.575
	041		1.750		411		1.574
	241		1.749	1	141	1.573	1.573
	013		1.748		411		1.572
	213		1.746		341		1.572
	410		1.743		150		1.567
	421		1.734		321		1.563
	321		1.734		421		1.563
	420		1.722		410		1.547
	320		1.721	0.5	250	1.544	1.546
	232		1.708		323		1.538
	332		1.707				

TABLE 6 (Continued)

<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>	<i>I</i>	<i>hkl</i>	<i>d meas.</i>	<i>d calc.</i>
1	223	1.537	1.537	1	510	1.389	1.389
0.5	401	1.521	1.519		150		1.388
	033		1.515		423		1.382
	042		1.511		323		1.382
	151		1.510		233		1.382
	342		1.510		403		1.379
	242		1.510		233		1.379
	142		1.509		241		1.378
2	{ 050	1.507	{ 1.506		441		1.378
	{ 133		{ 1.506		142		1.378
	{ 233		{ 1.506		351		1.377
	{ 332		{ 1.503	9	{ 151	1.377	{ 1.377
	{ 151		{ 1.501		{ 342		{ 1.377
4	{ 251	1.501	{ 1.501	7	{ 442	1.376	{ 1.376
	{ 432		{ 1.501		{ 242		{ 1.376
	{ 213		{ 1.501		114		1.371
4	313	1.498	1.498		114		1.371
	431		1.490		331		1.369
	331		1.488		501		1.368
1	{ 312	1.480	{ 1.480		531		1.368
	{ 203		{ 1.480		252		1.366
	133		1.478		004		1.366
	133		1.477		152		1.365
5	{ 412	1.476	{ 1.476		204		1.364
	{ 330		{ 1.476		014		1.357
	240		1.474		214		1.356
	440		1.474		412		1.354
3	{ 441	1.473	{ 1.474		152		1.352
	{ 251		{ 1.474		{ 530		{ 1.351
	{ 241		{ 1.473		{ 512		{ 1.351
	051		1.473	1	{ 322	1.351	{ 1.351
	123		1.465		{ 052		{ 1.351
	223		1.465		422		1.350
1	350	1.452	1.452		522		1.348
0.5	{ 033	1.435	{ 1.436	1	{ 422	1.348	{ 1.348
	{ 333		{ 1.435		{ 243		{ 1.348
	051		1.432		043		1.347
	351		1.431		500	1.341	1.341
	411		1.417	4	{ 143	1.335	{ 1.335
1	{ 511	1.415	{ 1.415	2	{ 143		{ 1.334
	{ 521		{ 1.415		014		1.331
	{ 421		{ 1.415		214		1.329
	213		1.408		352		1.325
	413		1.404		252		1.325
	232		1.402		133		1.321
	332		1.399		450		1.320
2	{ 104	1.393	{ 1.394				
	{ 420		{ 1.393				
	520		1.393				

TABLE 7
Unit-cell parameters of kyanites, 25°C

	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	α	β	γ	<i>V</i> , Å ³	<i>V</i> , cm ³ /mol
Burnsville, North Carolina	7.123 ± 0.002	7.844 ± 0.002	5.568 ± 0.002	89°54' ± 05'	101°13' ± 05'	105°59' ± 05'	292.93	44.121
Burnsville,* North Carolina	7.121 ± 0.002	7.846 ± 0.002	5.577 ± 0.005	89°58' ± 05'	101°09' ± 05'	106°00' ± 05'	293.40	44.191
Radium Hill, South Australia USNM No. R10542	7.123 ± 0.002	7.850 ± 0.002	5.560 ± 0.002	89°53' ± 05'	101°17' ± 05'	105°56' ± 05'	292.74	44.092
Windham, Maine USNM No. 9248	7.123 ± 0.002	7.850 ± 0.002	5.555 ± 0.002	89°51' ± 05'	101°18' ± 05'	105°57' ± 05'	292.47	44.051
Minas Gerais, Brazil USNM No. R9262	7.124 ± 0.002	7.850 ± 0.002	5.567 ± 0.002	89°55' ± 05'	101°16' ± 05'	106°00' ± 05'	293.09	44.145
Koli, Finland	7.123 ± 0.002	7.848 ± 0.002	5.572 ± 0.002	90°04' ± 05'	101°10' ± 05'	105°59' ± 05'	293.28	44.173
Koli, Finland*	7.120 ± 0.006	7.845 ± 0.006	5.571 ± 0.006	89°57' ± 10'	101°9' ± 10'	106°00' ± 15'	293.02	44.134
Bark- hamstead, Connecticut USNM No. R3743	7.121 ± 0.002	7.860 ± 0.002	5.586 ± 0.002	90°04' ± 05'	101°08' ± 05'	105°56' ± 05'	294.56	44.366

* Single crystal measurements, by quartz-calibrated precession photographs

Mean volume (powder data, excluding Barkhamstead, Conn.) = 44.116 ± 0.021 cm³/mol

Range 44.051–44.173 (powder data, excluding Barkhamstead, Conn.)

Standard deviation (powder data, excluding Barkhamstead, Conn.) = 0.047 cm³/mol

MEASUREMENTS AT HIGH TEMPERATURES

The high-temperature measurements were made on a heating stage mounted on a focusing diffractometer. A detailed description will appear elsewhere. The powdered sample is smeared on a mullite plate and heated between two parallel, flat heaters arranged perpendicular to the sample surface. The temperature of the sample is measured to within 1°C by a thermocouple which is imbedded in the mullite plate with its junction at the surface of the plate in the center of the sample. The thermocouple is calibrated against the thermal expansion and melting point of pure silver.

The heating stage is operated in vacuo; X-rays enter the vacuum chamber through aluminum foil and exit through a nickel window which also serves as

TABLE 8

Unit-cell edges of andalusite and sillimanite at high temperatures

Temperature °C	a, Å	b, Å	c, Å	Volume Å ³	Volume cm ³ /mol
Andalusite, Minas Gerais, Brazil (USNM.R2717)					
17	7.7939	7.8972	5.5565	342.00	51.511
25	7.7950	7.8996	5.5580	342.25	51.549
127	7.8036	7.9008	5.5630	342.98	51.659
213	7.8125	7.9080	5.5656	343.85	51.790
314	7.8229	7.9136	5.5714	344.91	51.950
416	7.8322	7.9200	5.5792	346.08	52.126
517	7.8424	7.9284	5.5852	347.27	52.305
616	7.8540	7.9340	5.5920	348.46	52.484
739	7.8682	7.9608	5.6010	350.83	52.841
870	7.8839	7.9688	5.6120	352.58	53.105
1008	7.9008	7.9820	5.6226	354.58	53.406
Sillimanite, Williamstown, South Australia (USNM.R10532)					
20	7.4808	7.6708	5.7690	331.05	49.862
25	7.4817	7.6712	5.7693	331.12	49.873
159	7.4832	7.6764	5.7725	331.60	49.945
265	7.4844	7.6829	5.7760	332.12	50.023
369	7.4868	7.6890	5.7780	332.62	50.099
464	7.4898	7.6951	5.7825	333.27	50.196
572	7.4935	7.7038	5.7861	334.02	50.309
688	7.4988	7.7120	5.7905	334.87	50.437
797	7.5037	7.7198	5.7945	335.66	50.556
932	7.5100	7.7351	5.8009	336.98	50.755
1055	7.5163	7.7464	5.8090	338.22	50.942

a filter for copper radiation. Measurements of the thermal expansion of silver and sodium chloride have shown that, once the heating stage is aligned at room temperature, it does not require realignment at high temperatures. In the present work, any dilution of the sample by an internal standard was avoided in order to obtain the greatest possible intensity. The stage was aligned at room temperature and the peaks to be measured were scanned several times. If the mean position of the peaks differed by more than 0.03 degrees 2θ from

TABLE 9

Unit-cell parameters of kyanite from Koli, Finland, at high temperatures

Temperature °C	a, Å	b, Å	c, Å	α	β	γ	Volume Å ³	cm ³ /mol Volume
25	7.123	7.848	5.572	90° 04'	101° 10'	105° 59'	293.28	44.173
168	7.130	7.856	5.577	90° 04'	101° 09'	106° 00'	294.11	44.298
281	7.136	7.862	5.582	90° 05'	101° 08'	106° 01'	294.83	44.407
406	7.144	7.870	5.591	90° 02'	101° 08'	106° 03'	295.93	44.572
554	7.155	7.880	5.600	90° 00'	101° 09'	106° 05'	297.18	44.761
685	7.164	7.889	5.608	89° 58'	101° 10'	106° 06'	298.30	44.929
862	7.179	7.902	5.621	89° 52'	101° 13'	106° 09'	299.97	45.181
1055	7.192	7.916	5.631	89° 51'	101° 12'	106° 10'	301.59	45.425

TABLE 10

Constants in the expression for molar volume of andalusite, kyanite
and sillimanite from 298°K to 1328°K

	A, cm ³ /mol	B, cm ³ /mol	C, cm ³ /mol ² °K	D, cm ³ /mol(°K) ²	Standard deviation cm ³ /mol
Andalusite, Minas Gerais (USNM R3717)	71.528	50.845	1.4099x10 ⁻⁸	4.3742x10 ⁻⁷	0.023
Kyanite, Koli, Finland	91.516	43.408	1.5561x10 ⁻⁸	-0.6514x10 ⁻⁷	0.006
Sillimanite, South Australia (USNM R10532)	1.6769	49.758	0.2073x10 ⁻⁸	5.1276x10 ⁻⁷	0.006

the positions previously found by measurement on a conventional stage with an internal standard, the heating stage was realigned. When a difference less than 0.03 degrees 2 θ was achieved, the run was made and the high-temperature results were adjusted by the amount of the difference at room temperature.

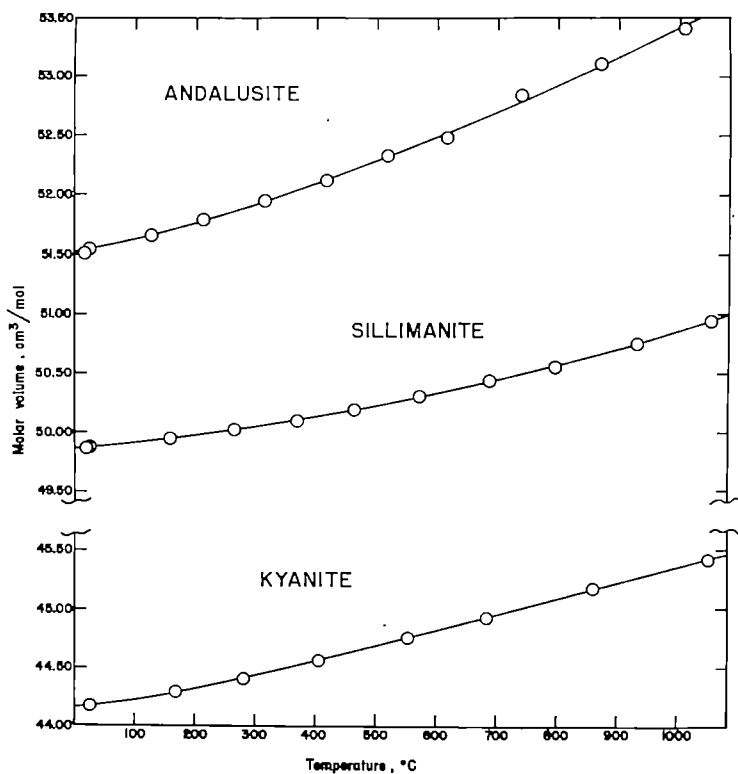


Fig. 1. Volumes of andalusite, sillimanite, and kyanite from room temperature to 1050°C.

Measurements were made at irregular temperature intervals and in random order to permit evaluation of any irreversible changes occurring in the sample.

Unit-cell parameters of the andalusite from Brazil were obtained at high temperatures from the (301), (031), (002), and (004) reflections; those of kyanite from Finland from the (112), (311), (140), (311), (050), and (500) reflections; and those of sillimanite from the (400), (420), (240), and (004) reflections. The results are given in tables 8 and 9. Noteworthy features of the measurements are the relatively large expansion of the a axis of andalusite, the relatively small expansion of the a axis of sillimanite, and the small but regular changes in the axial angles of kyanite. The smoothness of the data for kyanite again indicates that the powder method is free from accumulation of random experimental error.

To calculate the thermal expansion, it is necessary to find the derivative of the molar volume with respect to temperature. Direct numerical differentiation of the data is to be avoided because it leads to magnification of experimental error. Instead, the volumes were expressed by the function

$$V = A/T + B + CT + DT^2$$

where V is molar volume and T is absolute temperature. The constants A , B , C , and D were found by the method of least squares. This functional form was chosen because it had previously been found to represent the volumes of a wide variety of substances as a function of temperature, and also because it leads to a curve of thermal expansion vs temperature of the shape usually observed. The thermal expansion can be found by differentiating this function analytically.

Results of the calculations are presented in tables 10 and 11 and in figures 1 and 2. The volumes given in table 11 are the values calculated from the expression given above. The derivative of the volume with respect to temperature

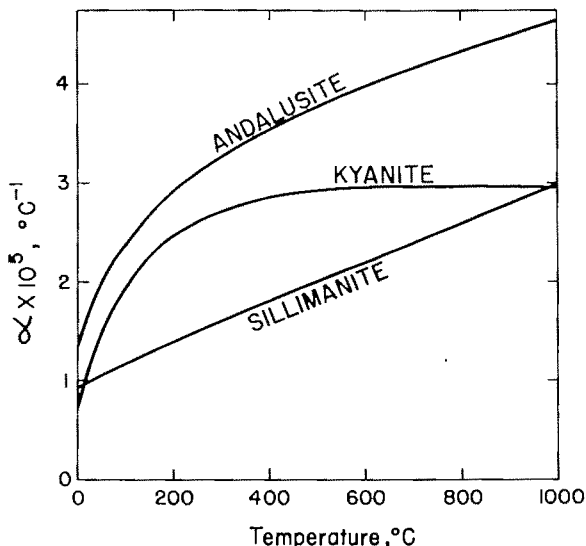


Fig. 2. Variation in the coefficient of volume thermal expansion (α) against temperature for andalusite, kyanite, and sillimanite.

appears in a number of thermodynamic relations, and hence it is given in table 11 along with the thermal expansion $\alpha_V = V^{-1} (\partial V / \partial T)_P$.

Of the curves of thermal expansion shown in figure 2, only that for andalusite has the shape found for simple substances such as periclase or diamond, and for garnets (Skinner, 1956, 1957). The constancy of the thermal expansion of kyanite at high temperatures may well result from uncertainty in the measurements of volume above 685°C. The nearly linear relation between thermal expansion and temperature found for sillimanite could be explained if its effective Debye temperature were lower than those of the other polymorphs, but this explanation is not in accord with the heat-capacity data (Todd, 1950).

It is of interest to compare the data for the aluminosilicates at high temperature with data for 1 mole of quartz plus 1 mole of corundum, since the thermodynamic properties of the compounds are close to the properties of this mixture of the oxides. The total molar volume of the oxides is 48.26 cm³/mol at 25°C, 49.14 cm³/mol at 500°C, and about 50 cm³/mol at 1000°C (data for quartz taken from Jay, 1933; data for corundum from Swanson and Fuyat, 1953, and Austin, 1931). These values are fairly close to the data for sillimanite; they are also close to the mean of the volumes of andalusite and kyanite. The thermal expansion of quartz plus corundum is 2.4×10^{-5} °C⁻¹ at 25°C, which is higher than the expansion of any of the aluminosilicates. At higher temperatures the thermal expansion of quartz plus corundum is strongly influenced by the anomalous expansion of quartz below the α - β transition and by the small, negative expansion of β -quartz. These anomalies also affect the volumes of the mixture, but to a much lesser extent than in quartz alone.

The slopes of the equilibrium curves between the polymorphs of Al₂SiO₅ on the pressure-temperature plane can be calculated by combining the present data with the entropies given by Todd (1950). Todd considers that his results are accurate to within about 0.1 cal/mol°C. The slopes calculated at 25°C and atmospheric pressure are 21.2 bars/°C for the kyanite-sillimanite boundary, 12.8 bars/°C for the andalusite-kyanite boundary, and -17.7 bars/°C for the andalusite-sillimanite boundary. These slopes must be corrected for differences in thermal expansion, compressibility, and heat capacity before they can be applied to conditions of higher pressure and temperature.

The correction for thermal expansion is greatest for the andalusite-sillimanite boundary. Above 100°C the difference in volume increases by nearly 0.1 cm³/mol for each 100°C increase in temperature. This is about 6 percent of the difference in volume at 25°C. The effect of pressure on ΔS , the entropy change of the reaction, is also dependent on the thermal expansion through the Maxwell relation $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$. According to the present data, ΔS decreases by about 3 percent per thousand bars for the andalusite-sillimanite boundary. Since the slope of the equilibrium curve is negative, these corrections are additive and the phase boundary may be markedly curved. For the other equilibrium curves this correction is less important both because of the smaller differences in thermal expansion and because of the larger changes in volume and entropy.

TABLE II
Molar volumes and thermal expansions of andalusite, kyanite and sillimanite at high temperatures

Temperature °C	Andalusite			Kyanite			Sillimanite		
	V cm ³ /mol	$\left(\frac{\partial V}{\partial T}\right)_P$ cm ³ /mol°C	α_P °C ⁻¹	V cm ³ /mol	$\left(\frac{\partial V}{\partial T}\right)_P$ cm ³ /mol°C	α_P °C ⁻¹	V cm ³ /mol	$\left(\frac{\partial V}{\partial T}\right)_P$ cm ³ /mol°C	α_P °C ⁻¹
0	51.525	0.689x10 ⁻³	1.34x10 ⁻³	44.164	0.293x10 ⁻³	0.66x10 ⁻³	49.859	0.465x10 ⁻³	0.93x10 ⁻³
100	51.624	1.222x10 ⁻³	2.37x10 ⁻³	44.225	0.850x10 ⁻³	1.92x10 ⁻³	49.912	0.578x10 ⁻³	1.16x10 ⁻³
200	51.761	1.504x10 ⁻³	2.91x10 ⁻³	44.323	1.085x10 ⁻³	2.45x10 ⁻³	49.975	0.685x10 ⁻³	1.37x10 ⁻³
300	51.921	1.693x10 ⁻³	3.26x10 ⁻³	44.438	1.203x10 ⁻³	2.71x10 ⁻³	50.048	0.790x10 ⁻³	1.58x10 ⁻³
400	52.098	1.841x10 ⁻³	3.53x10 ⁻³	44.562	1.266x10 ⁻³	2.84x10 ⁻³	50.133	0.894x10 ⁻³	1.78x10 ⁻³
500	52.289	1.966x10 ⁻³	3.76x10 ⁻³	44.691	1.302x10 ⁻³	2.91x10 ⁻³	50.227	0.997x10 ⁻³	1.99x10 ⁻³
600	52.491	2.080x10 ⁻³	3.96x10 ⁻³	44.822	1.322x10 ⁻³	2.95x10 ⁻³	50.332	1.100x10 ⁻³	2.19x10 ⁻³
700	52.704	2.186x10 ⁻³	4.15x10 ⁻³	44.955	1.333x10 ⁻³	2.96x10 ⁻³	50.447	1.203x10 ⁻³	2.39x10 ⁻³
800	52.928	2.286x10 ⁻³	4.32x10 ⁻³	45.088	1.337x10 ⁻³	2.96x10 ⁻³	50.573	1.306x10 ⁻³	2.58x10 ⁻³
900	53.162	2.384x10 ⁻³	4.48x10 ⁻³	45.222	1.337x10 ⁻³	2.96x10 ⁻³	50.709	1.409x10 ⁻³	2.78x10 ⁻³
1000	53.405	2.479x10 ⁻³	4.64x10 ⁻³	45.356	1.334x10 ⁻³	2.94x10 ⁻³	50.855	1.512x10 ⁻³	2.97x10 ⁻³

The slope of the kyanite-sillimanite boundary determined experimentally at high pressure and temperatures does not agree well with the value calculated above (Clark, 1961). The correction for thermal expansion is too small to explain the discrepancy, and this is probably also true for differences in compressibility, assuming that they can be estimated within an order of magnitude. It is possible that differences in heat capacity may account for the curvature required to bring the two sets of data into agreement, but the heat capacity measurements are old and of doubtful reliability. New high-temperature heat capacities must be obtained before the slopes of the phase boundaries can be reliably calculated at high temperatures and pressures.

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A CLIMATIC SEQUENCE FROM TWO NEVADA CAVES

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ABSTRACT. Fishbone and Guano Caves, cut in granite by pluvial Lake Lahontan, were exposed for animal and human occupation about the time of the Two Creeks interstadial. Aside from the usual irregularities due to habitation, modern disturbance has made it impossible to secure continuous stratigraphy in the samples furnished by P. C. Orr. However, by combining radiocarbon dates and study of the sediments as well as statistical analysis of the included pollen, a profile consonant with known climatic history since about 15,000 years B.P. has been obtained. A climax of aridity occurred between 6000 and 7000 B.P. shortly following the undoubted evidence of Pleistocene horse and camel. A less extreme aridity developed about 3200 B.P.

Interesting evidence of climatic change before 15,000 is present, but its chronology must await study of cores from the sediments of Lake Winnemucca.

In 1954 we received from P. C. Orr of the Western Speleological Institute seven samples of floor sediment, four from Guano Cave, three from Fishbone Cave, in Pershing County, Nevada. These caves had been cut in granite by Pluvial Lake Lahontan and lie at the north end of dry Lake Winnemucca at an elevation of approximately 4060 feet, some 270 feet above the present level of Pyramid Lake.

It was first believed that Guano lay below Fishbone, but later measurement places them at the same altitude. The longer persistence of waterlaid sediments in Guano may have been due to the formation of a barrier across the mouth of Fishbone. Orr (1956) has described the archaeology of Fishbone and later (Broecker and Orr, 1958) its geological history. He designates six levels in Fishbone and seven in Guano. His correspondence describes them as follows:

GUANO CAVE

- Level 1 Top. About 3 inches of fine windblown dust mixed with rat and bat guano. No artifacts. Disturbed.
- Level 2 Hard-packed dust with some rat and bat guano and dung of large mammals. No artifacts. Depth not given.
- Level 3 Loose dirt, straw and chaff, ash, and some dung. Upper habitation level, artifacts present. Depth not given.
- Level 4 Similar to Level 3, not always distinct from it. Hard-packed layers in both. Middle occupation layer. Depth not given, but deeper than Level 3.
- Level 5 More sand and gravel, lighter in color than preceding. Some guano, few artifacts; lower habitation level. Depth not given.
- Level 6 Compact layer of silt and plant remains. Depth not given.
- Level 7 Sand and gravel containing brush and small mammal bones.

FISHBONE CAVE

- Level 1 Top. 3 to 18 inches of windblown dust, rat and bat guano. No artifacts.
- Level 2 3 to 12 inches, similar to preceding, but more compact.
- Level 3 24 to 60 inches of loose, windblown dust, rat and bat guano, grass, sticks, charcoal, ash, food caches, human burials, and artifacts. Horse and camel bones present, but these may have been dug up from layer below.

Level 4 12 to 24 inches similar to Layer 3 but more clean sand. Brush, bones of horse, camel, marmot, and man. Burned brush, guano, and human bones. Camel and horse bones split.

Level 5 Thin layer of broken tufa, evidently fallen when sand below it was washed out.

Level 6 Lake sand and gravel. No artifacts or mammal bones.

The samples received by us were as follows:

GUANO CAVE

Field

No.	Description	Our Notation
P3d-1	Level 1 — Loose dust and guano	G1
P3d-2	Level 2 — Compact dust and guano	G2 no sample
P3d-3	Level 3 — Black dust, artifacts	G3
P3d-4	Level 4 — Dust, debris, artifacts	G4 no sample
P3d-5	Level 5 — Sand, artifacts	G-5
P3d-6	Level 6 — Sand, trampled	G6
P3d-7	Level 7 — Sand, small bones	G7 no sample

FISHBONE CAVE

P3e-1	Level 1 — Loose dust and guano	F1 no sample
P3e-2	Level 2 — Compact dust and guano	F2 no sample
P3e-3	Level 3 — Dust, guano, artifacts	F3
P3e-4	Level 4 — Same with horse and camel bones	F4
P3e-5	Level 5 — Fallen tufa	F5 no sample
P3e-6	Level 6 — Silt, sand, shell	F6

TABLE 1

Pollen analysis of Levels 1 to 6, Fishbone and Guano

	FISHBONE						GUANO					
	F1	F2	F3	F4	F5	F6	G1	G2	G3	G4	G5	G6
Abies			01				21		05		03	01
Picea							13		03		08	+
Pinus			32	16		26	50		44		74	60
Alnus			+			+			01			
Quercus			01	01		02	02		03		01	02
Subtotal			34	17		29	86		56		86	63
Artemisia Subtotal			08	08		12	02		17		+	08
Compositae			04	58		06			03			05
Epilobium			01	02		01	01		+			+
Gramineae									02		04	
Subtotal			05	60		07	01		05		04	05
Chenopod.			53	15		52	11		22		08	23
Ephedra						+	02		01		01	01
Subtotal			53	15		52	13		23		09	24
?											01	
Total count			472	344		626	133		865		410	928

Enough pollen was recovered to warrant further study under better stratigraphic control. On request, P. C. Orr supplied us with a suite of six samples representing 54 inches beginning at the top of the occupational zone on the left side of Guano, and an additional suite of three samples taken 5 feet east, carrying the sampling down to 100 inches. The bottom sample of the first lot and the top sample of the second were thought to be equivalent. A third suite of five samples from the right side of the cave, extending from 12 to 54 inches in depth, and an equivalent to the 54-inch sample taken five feet away at a depth of 40 inches were also received.

From Fishbone which had meanwhile been disturbed by vandals, Orr was able to supply us with only six samples from a 60-inch column beginning near the top of Level 6. Clearly the difficulties imposed by the original character of the sites were compounded by the impossibility of getting a continuous stratigraphy. The problem thus became one familiar to archeologists and paleontologists, that of developing a useful reconstruction out of fragments of physical evidence, despite serious gaps.

The second series of samples were as follows:

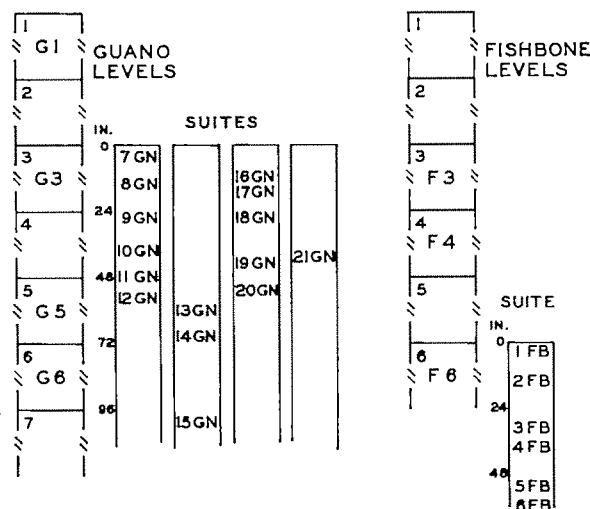
GUANO CAVE, LEFT SIDE. BEGINNING AT TOP OF LEVEL 3 (OCCUPATIONAL)

<i>Field No.</i>	<i>Description</i>	<i>Our Notation</i>
Guano 7*	0 to 6 inches Black dust	7 GN
Guano 8	12 to 18 inches " "	8 GN
9	24 to 30 inches " "	9 GN
10	36 to 40 inches Black, compact	10 GN
11	46 to 50 inches Sand	11 GN
12	54 to 58 inches "	12 GN
From 5 ft east of preceding		
13	58 to 64 inches Sand	13 GN
14	66 to 72 inches "	14 GN
15	98 to 100 inches Gravel	15 GN
From right side of cave		
16	12 inches Fire remains	16 GN
17	15 to 18 inches Silts and shell	17 GN
18	22 to 28 inches Sticks and dust	18 GN
19	42 to 47 inches Guano	19 GN
20	54 inches Sand	20 GN
Five feet from preceding		
21	40 inches Fire in sand	21 GN

FISHBONE CAVE, FROM TOP OF LEVEL 6

P3e6-1	4 inches Lake silts and shell	1FB
2	14 inches Silts, sand, shell	2FB
3	33 inches Fine silts and sand	3FB
4	38 inches No field descr.	4FB
5	54 inches Silt	5FB
6	60 inches Gravel	6FB

* Not to be confused with P3d-7, which is Level 7 in Guano.



The schematic relation of the various samples is shown in figure 1. No depth scale is available for samples representing the various levels. The depth

	7GN	8GN	9GN	10GN	11GN	12GN	13GN	14GN	15GN
	0-5"	12-18"	24-30"	36-40"	46-50"	54-58"	58-64"	66-73"	90-100"
<i>Abies</i>	02	01	01	+	+	01	+		+
<i>Juniperus</i>	01	02	02	+	02	03	12	03	01
<i>Libocedrus</i>			+		+	+			+
<i>Picea</i>	01	05	02	01	01	03	02	06	03
<i>Pinus</i>	13	11	19	03	07	25	29	63	15
<i>Alnus</i>			+	+			+		+
<i>Betula</i>	+		+				+		
<i>Juglans</i>				+					
<i>Quercus</i>	01		+	+	01	+	+		+
Subtotal	18	19	24	04	12	33	44	72	20
<i>Artemisia</i> Subtotal	08	13	14	03	26	17	18	08	14
<i>Ambrosia</i>		01	+	+		+	01		01
<i>Carices</i>	01		+			+	C		+
<i>Compositae</i>	05	07	04	01	04	03	04	06	04
<i>Epilobium</i>	01	01	+	+	+	01	+	02	01
<i>Gramineae</i>	30	02	01	+	01	04	14		01
<i>Polygonum</i>	+	02 T				+			+
Subtotal	37	13	07	02	05	08	19	08	07
<i>Cactaceae</i>									
<i>Chenopod.</i>	37	54	55	91	57	42	19	12	59
<i>Ephedra</i>		01	+		+				
Subtotal	37	55	55	91	57	42	19	12	59
?	03	03	07	02	08	03	02	0	02
Total count	312	297	851	1608	578	684	460	35	531

C = *Cercocarpus*; G = *Gilia*; T = *Typha*

scale for Guano (7GN to 21GN) begins at the top of Level 3, but the diagram is not intended to show correlations below this. The depth scale for Fishbone (1Fb to 6Fb) begins at the top of Level 6.

Pollen percentages have been grouped and sub-totaled in the tables into four divisions: Tree or Arboreal (AP), *Artemisia*, Grassland, Desert, because this represents the altitudinal zonation of the area in descending order, and it has been shown that these zones move up and down in response to climatic change (Clisby and Sears, 1956; Roosma, 1958). Bar graphs were prepared for each spectrum to show the proportion of each of these four zones in the hope that by comparing them a reliable arrangement could be made, as the stratigraphic data were not continuous. Unfortunately the graphs showing transition between the two extremes—Arboreal and Desert—gave no clue as to the direction in which climate was shifting at a particular time.

Meanwhile an increasing number of radiocarbon dates became available, (Broecker and Orr, 1958) and to these Broecker generously added a critical one for the desert maximum shown by Sample 18 GN. These dates are as follows:

Sample	R.C. No.	Time B.P.	Remarks
18GN	L-356B	3,200 $\pm$ 130	
10GN	L-596	6,500 $\pm$ 150	
F4	L-289KK	7,380 $\pm$ 500	
F4B	L-245	11,200 $\pm$ 250	Base of habitation, no pollen sample
T	L-289C	11,700 $\pm$ 500	Tufa from entrance barrier of Fishbone, no pollen sample
F5	L-289D	14,800 $\pm$ 500	Fallen tufa, no pollen sample
F6	L-289P	15,130 $\pm$ 550	Shells from lake sediments, no pollen sample
1FB	L-289	15,760 $\pm$ 700	

Two other dates are of interest in this connection (Flint and Gale, 1958; Roosma, 1958). They are 10,500 $\pm$ 560 (C-894) for the top of an organic layer below 90 ft of salt at Searles Lake, California, and 21,200 $\pm$ 2170 (Y-267) for the bottom. This layer shows a considerably higher proportion of arboreal pollen than the sediment above it and is contemporaneous with active Wisconsin glaciation, demonstrating the influence of its climate at remote distance from the glacial margin.

In addition to the above dates, helpful suggestions were received from P. C. Orr. Finally we re-examined the sediments themselves, noting especially the character and condition of mineral materials, presence and condition of ostracod and gastropod shells, and fragments of bone, charcoal, and flint. And, as the proportion of tree pollen is a sufficient indicator of climatic conditions in this area, we plotted it (fig. 2) after arranging the samples in an order indicated by the other information at hand.

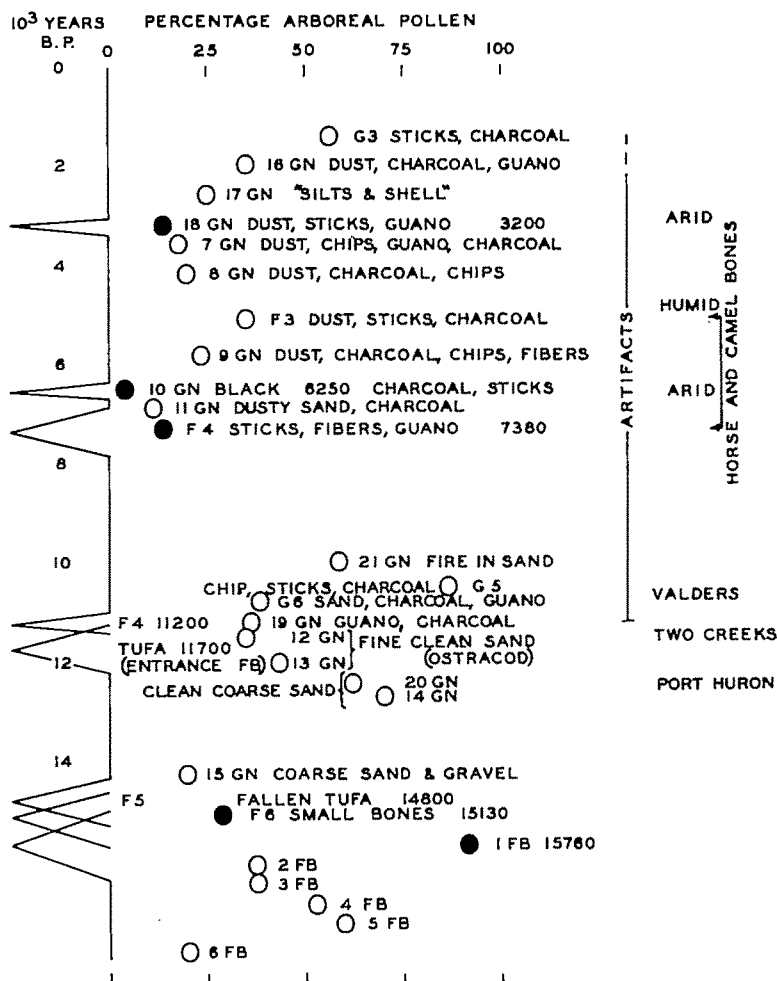


Fig. 2. Percentages of arboreal pollen. (See text for explanation.)

At the left in figure 2 is a time scale in thousands of years B.P. with available radiocarbon dates pinpointed and bracketed to show limits of probable error. Against this scale percentages of tree or arboreal pollen (AP) are plotted, with black circles to indicate dated samples, open circles those not dated. Each circle is followed by its sample number (see preceding tables) and brief notes from our microscopic examination of the sediments. Additional information at the right is self-explanatory.

Three radiocarbon dates have no supporting pollen spectra. F4 at circa 11,200 records the occupation of Fishbone by animals and man (Broecker and Orr 1958, p. 1026). T at circa 11,700 is from tufa at the entrance of Fishbone, indicating the presence of water at that level then. F5 at circa 14,800 is from a broken layer of tufa that formed on top of sand that was later washed

TABLE 3

Pollen analysis of suites from right side of Guano

	16GN	17GN	18GN	19GN	20GN	21GN
	12"	15-18"	22-28"	42-47"	54"	40"
Abies	+	+	01	+	01	
Juniperus	02	01	02	02	27	02
Libocedrus			+	+	02	
Picea	03	04	01	05	07	11
Pinus	30	20	11	26	23	43
Alnus	+	+	+			01
Betula				+	+	
Quercus	+		+	+	+	01
Subtotal	35	25	16	34	62	58
Artemisia Subtotal	21	13	10	33	10	24
Ambrosia	+	01	+	+	+	
Carices	01		+	+		
Compositae	06	14	03	16	04	03
Epilobium	01	01	01	03		01
Gramineae	04	+	04	01	13	03
Polygonum			+ G	+ G	+ G	
Subtotal	12	16	08	21	17	07
Cactaceae						
Chenopod.	32	47	66	12	10	11
Ephedra		+	+		+	
Subtotal	32	47	66	12	10	11
?	05	+	03	06	04	01
Total count	314	1029	1245	605	430	161

G = Gilia; C = Cercocarpus

out as the water level receded, causing the tufa to collapse (Broecker and Orr, p. 1026). As tufa forms as an evaporite and/or from organisms growing in shallow calcareous water, the association of both tufa samples with times of low forest pollen count is reasonable. Such association is further supported for F5 by the record of F6 at circa 15,130 when the cave floor was either exposed or so shallowly covered that owl pellets dropped on it remained in place (Orr, 1956). Sample T corresponds closely in time to the Two Creeks interstadial circa 11,500 and shortly precedes the drying of the cave that permitted its occupation.

So far as the open, undated circles are concerned, we have been obliged to space them according to our best judgment. In this we have been guided by their bracketing dates and their stratigraphic positions, so far as our information permits, also by the character of their sedimentary matrices, as figure 2 makes evident. Certainly the transition from sediments deposited by water to those that are subaerial is clear, as is the transition from the older, coarser to the finer, later subaqueous materials.

Given the gaps that exist in the record, and with due regard to all data available to us, we have associated undated spectra of relatively high forest pollen content with times known to have been relatively moist. Thus we place G3 with reference to the moister trend that began about the time of the

TABLE 4
Pollen analysis of suite from Level 6, Fishbone

	1Fb 4"	2Fb 14"	3Fb 33"	4Fb 38"	5Fb 54"	6Fb 60"
Abies	01	-	+		+	+
Juniperus	01	03	06	01	03	02
Libocedrus			+			+
Picea	07	04	01	04	05	01
Pinus	84	32	30	49	52	16
Alnus	+	+				
Juglans		+				
Quercus						01
Sub total	93	39	38	54	60	20
Artemisia Subtotal	02	23	35	26	29	26
Ambrosia	01	01	03	02	01	01
Carices				01	+	01 G
Compositae	01	18	06	11	03	28
Epilobium		01	01			01
Gramineae	+	02	04	01	03	03
Polygonum					+	01
Sub total	02	23	14	15	07	34
Cactaceae		+				
Chenopod.	02+	13	12	05	04	20
Ephedra	0	01	01			
Sub total	03	15	13	05	04	20
?	02	02	12	03	04	02
Total count	577	580	281	273	699	582

G = *Gilia*

Christian era. F3 is placed circa 5000 B.P. to correspond with the humid episode that followed 6000 and is confirmed by samples 9, 8, and 7GN lying above the dated sample 10GN. Although a good argument could be made for placing F3 much later (cf. 16GN), the breakdown of its spectrum in figure 3 as compared with that of 9GN leads us to place it as we have done. Also the presence of horse and camel bones, even though these may have been dug up by man from a short distance below, seems significant.

Similar reasoning has led us to associate the moist maximum of G5 with the Valders and that of 14GN with the Port Huron. The oldest and most extreme forest maximum, 1FB at 15,670, requires no further explanation for its placement. Evidently it corresponds with a time of glacial activity somewhere within the rather wide limits of its probable error. Stratigraphically it lies between two more arid intervals.

Concerning the lowest and oldest set of undated spectra, all we can be reasonably certain of is their sequence and their climatic significance. None of the other evidence available to us gives any clue as to their spacing on the time scale.

Fortunately, it should be possible to check and refine our reconstruction by coring and analysis of the sediments in the bed of Lake Winnemucca, which lies below these two caves. Such a project seems amply justified both from its climatic and archeological importance.

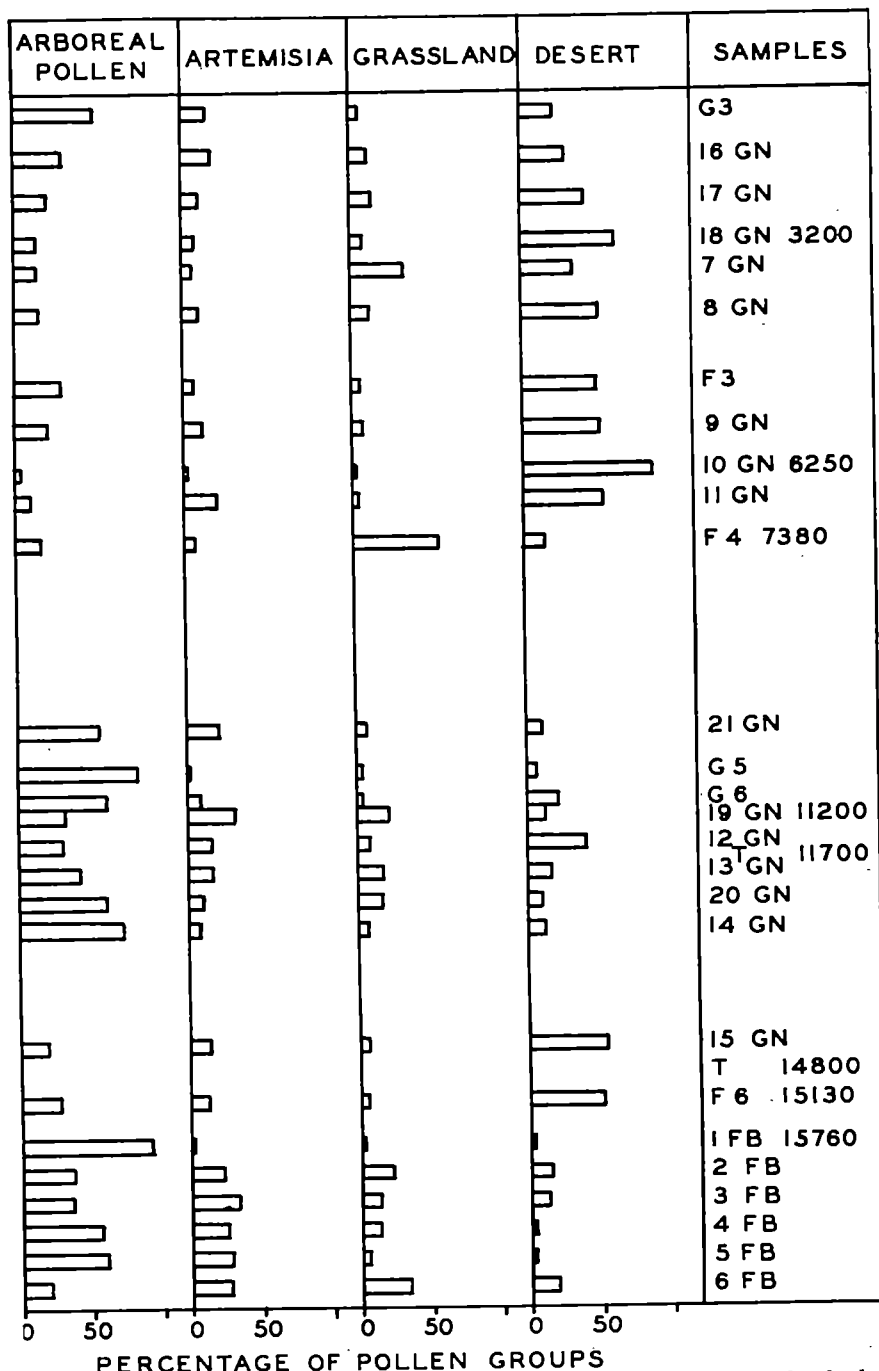


Fig. 3. Pollen percentages broken down into zonal groups. (See text for further details.) From Sears, P. B., 1961, Solar variations, climatic change, and related geophysical problems: *Annals of the New York Academy of Sciences*, volume 59, article 1.

Figure 3, representing the four-part profile based upon vegetation zones mentioned earlier, is chiefly of interest in showing the transitional character of Artemisia and Grassland between extremes of Forest and Desert.

In conclusion, our results indicate that the caves became habitable at about the time of the Two Creeks interval circa 11,500 B.P. and remained so thereafter, despite moist episodes until they were abandoned some time after 2000 years ago. The generally arid climate during this period of occupation reached an extreme at about 6250 B.P., whereas Pleistocene mammals survived to at least 7380 B.P.

ACKNOWLEDGMENTS

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A LATE WISCONSIN BURIED PEAT AT NORTH BRANCH, MINNESOTA*

MAGNUS FRIES,¹ H. E. WRIGHT, JR.² and MEYER RUBIN³

ABSTRACT. At North Branch peat began to accumulate after the Grantsburg lobe (Mankato substage) started to retreat. The radiocarbon dates on the peat and its contained wood (12,700 and 12,030 B.P.) indicate that the Mankato substage preceded the Two Creeks interstadial rather than followed it. The peat was thus formed during the early part of the Two Creeks interstadial. The pollen and macrofossils from the peat suggest a landscape marked by sedge swamps and probably spruce-tamarack swamps on a broad river floodplain, bounded by oak and ash and prairielike communities on upland sites. The climate seems to have been only slightly colder than today and probably drier.

The peat is overlain by sand that contains involuted layers of silt or clay rich in organic matter. These organic layers are believed to have formed as normal fine-grained sediment in quiet water. The pollen analysis indicates a vegetation dominated by pine and oak, typical of the postglacial. A radiocarbon date of 2520 B.P. for the upper part of the series of organic layers confirms the postglacial correlation. The folding of the layers into involutions must therefore have been produced without the aid of a permafrost base and may have resulted from localized annual frost connected with tussock growth of plants.

INTRODUCTION

The stratigraphic and paleobotanical study of the Two Creeks forest bed at the type locality in northeastern Wisconsin (Thwaites, 1943; Wilson, 1932, 1936) focused attention on the nature of the vegetation during the late Wisconsin interstadial intervals, and the early application of the radiocarbon dating technique to this site has made it a central point in any discussion of late Wisconsin chronology and biogeography for the Great Lakes region. The early assumption that the forest bed represented the time of ice retreat between Cary and Mankato ice advances was refuted by Thwaites (1946, p. 82), who held the opinion that the red clayey till above the forest bed was not necessarily correlative with the Mankato, and who therefore introduced the name Valders for this stratigraphic unit. The history of the correlation problem has been reviewed elsewhere (Wright, in press), and it is now believed that the place of the Two Creeks interstadial is between Mankato and Valders rather than between Cary and Mankato (Wright and Rubin, 1956).

Especially critical in this major revision in the late Wisconsin chronology are the relations in Minnesota, whence the term Mankato. The relations of the Cary and Mankato drifts are best seen in the area of the Anoka sandplain north of Minneapolis. The Cary ice of the Superior lobe, after forming the massive St. Croix moraine at its terminus near Minneapolis, retreated far enough to the north into the Lake Superior drainage basin to allow the cutting and then the abandonment of a series of drainage channels across the newly exposed terrain in eastern Minnesota (Wright, 1956). During the Mankato interval the Des Moines lobe, which occupied the Red River and Minnesota River valleys in western Minnesota, including the type locality of the Mankato itself, projected the Grantsburg sublobe eastward across this area just recently

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bared by the retreat of the Cary Superior lobe. The Mississippi River was dammed by the Grantsburg ice to form Glacial Lake Grantsburg, which had its outlet via the St. Croix River (Cooper, 1935). Retreat of the Grantsburg ice back toward the southwest allowed the lake to drain, and during the retreat the Mississippi River, still diverted eastward to the St. Croix River, built the vast Anoka sandplain over a triangular area 75 miles broad in eastern Minnesota (fig. 1).

The buried peat site of North Branch is located on the Anoka sandplain and thus records events starting at the time of retreat of the Mankato Grantsburg sublobe. The site was discovered in 1955 by R. S. Farnham of the Soils Division, University of Minnesota. Initially, the site was considered important because of the opportunity of obtaining a radiocarbon date for the late Mankato for comparison with C^{14} dates of the Two Creeks forest bed in Wisconsin (11,400 B.P.). The dates obtained from the buried wood and peat (12,700 and 12,030 B.P., see below) suggested that the Mankato was older rather than younger than the Two Creeks interstadial, as had previously been

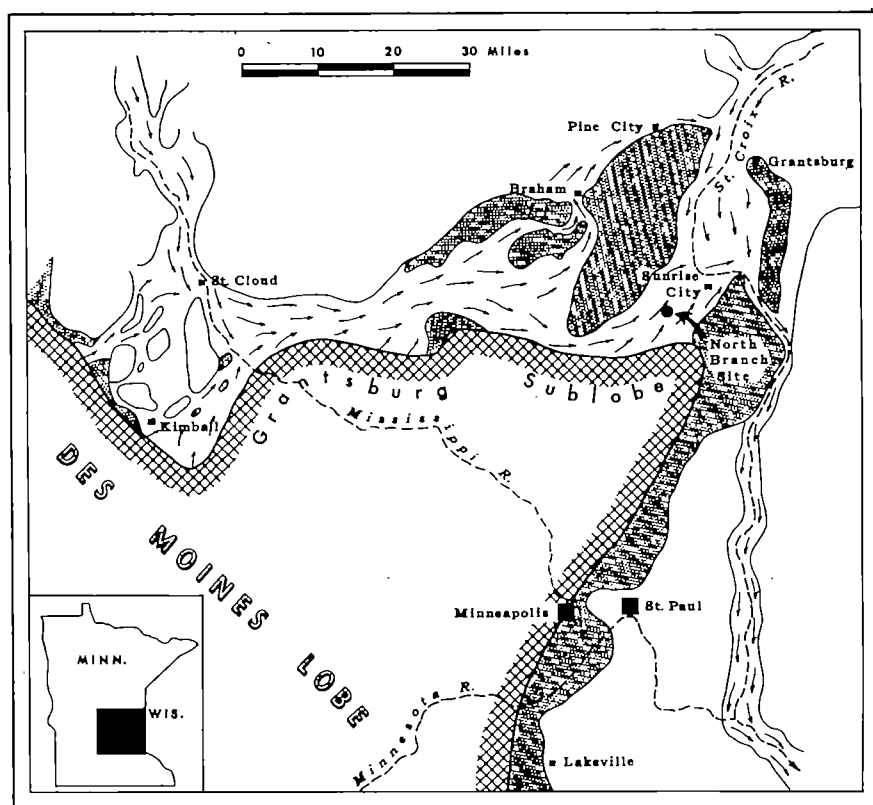


Fig. 1. Map showing location of North Branch site with reference to retreatal position of Grantsburg sublobe at time of formation of Anoka sandplain (small arrows from west to east). Stippled pattern indicates till deposited by Grantsburg sublobe at its maximum. (Redrawn by R. C. Bright from Cooper, 1935, fig. 24.)

assumed, and, along with other C^{14} dates associated with Mankato drift in eastern Minnesota, served as a principal impetus for the revision of the late Wisconsin chronology for the Great Lakes region (Wright and Rubin, 1956; Wright, in press).

A second feature of interest at the North Branch site is the strongly involuted layers of sand above the buried peat. Involutions of this type are generally considered to be indicative of permanently frozen ground, in this section possibly a record of a post-Mankato cold phase, i.e. the Valders in the revised chronology. Thereupon a pollen analysis of the complete profile was prepared to determine the nature of the late Wisconsin vegetation of the region, and an additional radiocarbon date was obtained to determine the age of the involutions.

In a recent article, Frye and Willman (1960) suggest dropping the term Mankato because it "introduces a complicating modification of both Mankato and Cary, [and] produces an unneeded substage". They have introduced the time-stratigraphic term "Woodfordian substage", to include all the time since the "Farmdalian substage" up to the "Two Creekan substage". This classification would do away with the terms Iowan, Tazewell, Cary, and Mankato. Despite the present lack of pedological and pollen-analytical evidence for climatic amelioration in the Cary-Mankato interval in the Great Lakes region, the geomorphic evidence in Minnesota (Wright, 1956) suggests significant ice retreat at this time, and the authors believe the terms Cary, Mankato, and Valders are still useful to refer to ice advances in Minnesota and adjacent regions, with the understanding that the Two Creeks interval separates the Mankato from the Valders rather than the Cary from the Mankato, as previously believed. Current mapping, pollen-analytical studies, and radiocarbon dating dedicated to this problem will certainly provide more precise data in the near future concerning the late Wisconsin history of this region.

The writers are obliged to Farnham for guidance to the site and for aid in the interpretation of some of the features, to numerous geological visitors who have offered candid opinions about the relations (among them F. M. Swain, Nicolas Prokopovich, Jean de Heinzelin, Friedrich Brandtner, Paul Woldstedt, Saskia Jelgersma), and to several students who have excavated and re-excavated the site in the course of field exercises (notably L. J. Maher, Jr., and John O'Brien). The pollen analyses were made by Fries in the Pollen laboratory of the Department of Geology, University of Minnesota, as a project supported by the Hill Family Foundation, St. Paul. The C^{14} analyses were made by Rubin at the U. S. Geological Survey, Washington, D. C.

LOCATION AND DESCRIPTION

The North Branch site is located 3.3 miles southeast of the village of North Branch, Chisago County, Minnesota, in the NE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 26, T.35N., R.21W., on the Forest Lake topographic quadrangle map of the U. S. Geological Survey (fig. 1). The section is exposed in a drainage ditch that carries water northward from a shallow depression for 600 feet to a small tributary of Hay Creek, which in turn flows to the St. Croix River (fig. 2). The site is 2 miles south of the terrace bluffs leading down to the St. Croix

River valley. The shallow depression is typical of the numerous small swamps and shallow lakes that dot the Anoka sandplain. Some are ice-block holes, some are blowouts, and some represent braids on the floodplain of the broad Mississippi River as it built the sandplain during its diversion eastward to the St. Croix River (Cooper, 1935). The intermittently wet part of the depression is about 5 acres in area at present. It is surrounded by a former swamp area of irregular branching shape that is somewhat drier and contains the buried peat site itself (fig. 2). The sandy "upland" on the north has an altitude of about 885 feet, or about 15 feet above the level of the center of the depression. This depression is now perennially dry because of the artificial drainage. The floor has only about a half-meter of sandy peat, so probably the depression has not often been wet.

The upland vegetation of today is characterized by scattered remnants of deciduous forest consisting of oak species (mostly *Quercus macrocarpa* and

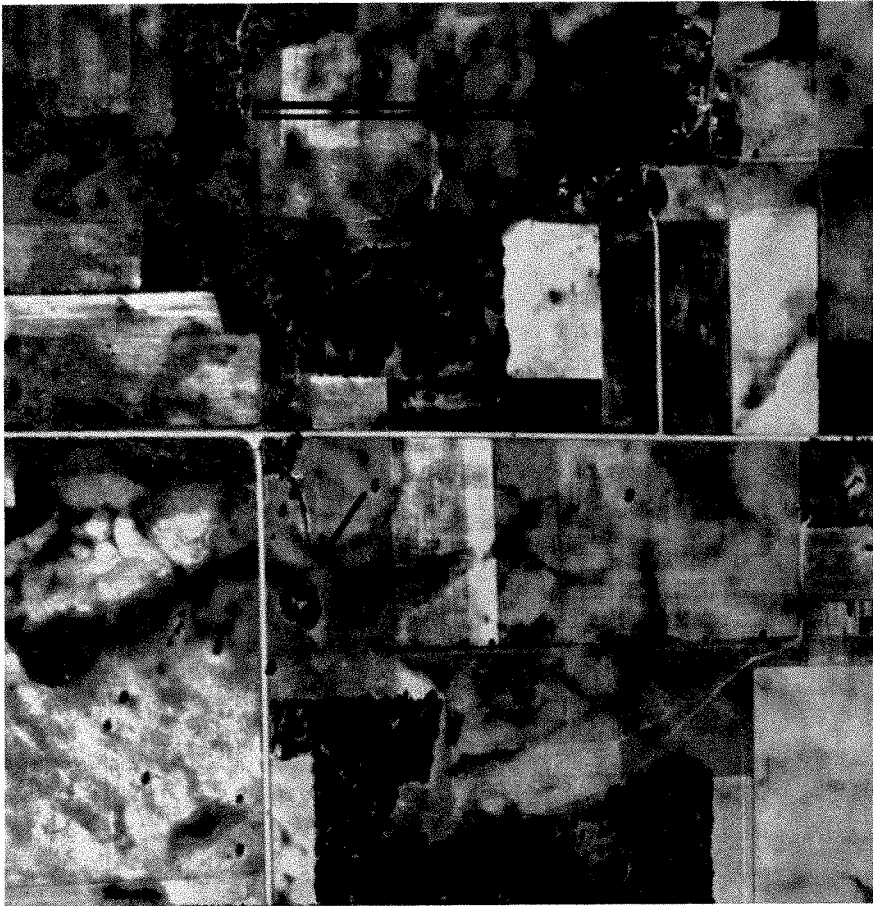


Fig. 2. Air photograph showing location of North Branch site (arrow) in drainage ditch. Shallow branching depressions are probably braids on glacial river floodplain, but deeper depressions may represent buried ice blocks. Black east-west double bar is $\frac{1}{4}$ mile long. U. S. Dept. Agriculture photograph 1938.

ellipsoidalis) and other hardwoods in a landscape with large open tilled and grazed areas. Most of the swamps are covered by sedge mat. In the vicinity and towards the south and southwest there are scattered small treeless areas or "oak openings" which are believed to be outliers of the prairie (Farnham, 1956, p. 61; Marschner, about 1930). According to Upham's map of the pre-settlement forest cover (1884, pl. 1), the area is situated a few miles outside of the southwestern limits of pines (mostly *Pinus strobus*), black spruce (*Picea mariana*), and balsam fir (*Abies balsamea*) but within the range of southernmost outliers of tamarack (*Larix laricina*). Thus it lies in the tension zones between the boreal coniferous forest, the deciduous hardwood forest, and the prairie.

The buried peat is found on the west bank of the drainage ditch and has a maximum thickness of 15 cm (figs. 3, 4). It is underlain by white or gray sand and grit, and is overlain by about 90 cm of weakly stratified medium to fine sand containing layers and lenses of brown peaty sand, black clay rich in organic matter, and, near the top, sand blackened with organic matter. One organic layer consists of a black waxy material on which Farnham obtained the following data: pH 5.2, organic matter 25%, free Fe and Al oxides 6.6%. The section is capped uncomformably by about 25 cm of laminated peaty sand.

The buried peat layer has a lenticular saucerlike form and is traceable for 9 m horizontally along the ditch face. It slopes gently upward and passes into an organic silt layer, which can be traced an additional 3 m to the north and 3 m south.

Some of the organic clay layers above the peat may be traced northward along the ditch for about 40 m, but they also gradually pinch out as the terrain rises into the low swell that borders the depression on the north and is transected by the ditch.

The sand is partly oxidized to yellow or brown to a depth of 1.2 m; the oxidation zones are discontinuous and controlled in part by the textures of the sand layers.

Between depths of about 25 and 100 cm the silt and sand layers are strongly involuted into bell-shaped folds (fig. 3), some of which are cut off at the necks to reveal spherical or pearshaped forms in cross-section. Inasmuch as the organic layers form a saucerlike structure, they become involved in the involution layer as they rise laterally to the requisite level.

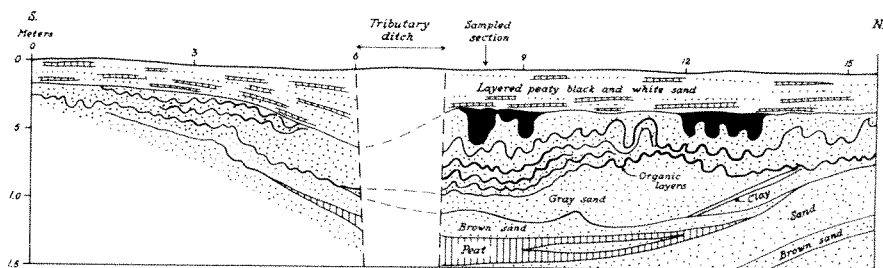


Fig. 3. Sketch of buried peat and involuted sand on west bank of drainage ditch at North Branch site.

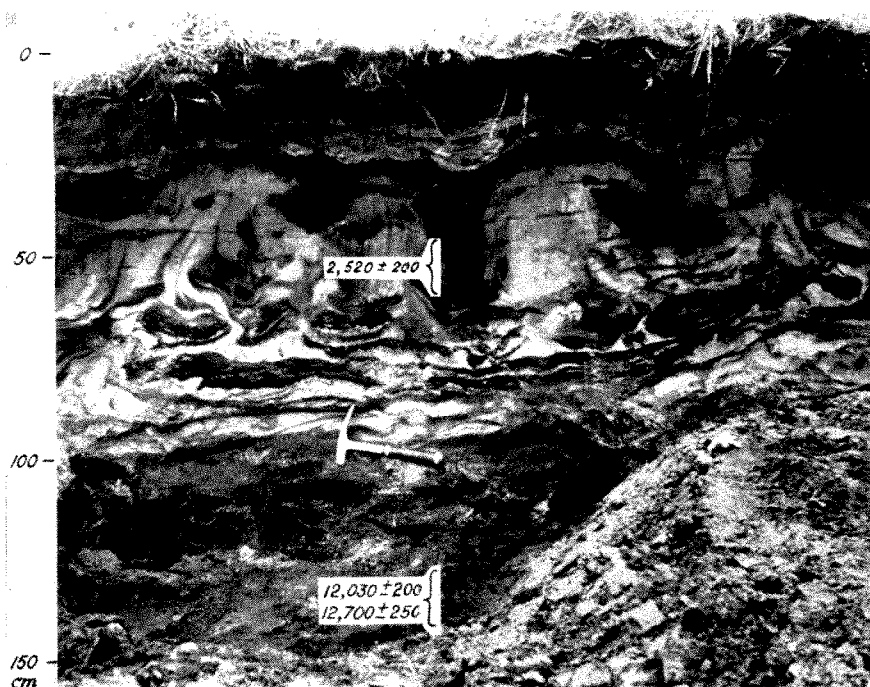


Fig. 4. The sampled section with buried peat (at the bottom) and involuted sand. Positions of samples for radiocarbon dating are marked. Cf. fig. 3.

ORIGIN OF SEDIMENTS

The buried peat contains a few very thin laminae of sand, some of the laminae being only a few grains thick. The peat itself is weakly laminated. These laminations, as well as the thin layers of organic clay above the peat, suggest that the sediment was deposited in water. The site may represent initially a small depression on a braided river floodplain. When the floodplain was abandoned after complete retreat of the ice, the depression was filled by inwash of sand and finer sediment. There may not necessarily be any relation between the depression in which the peat was formed and the present swamp, for the latter may be the result of later collapse over a buried ice mass.

The organic material in the silt and clay layers that are interbedded with the sand may also have been deposited along with the fine clastic particles when pools of water stood in the depression. An alternative explanation involves transport of the organic matter (including pollen grains) downward through the sands at a later time during the process of incipient soil formation. In this explanation, the organic matter was illuviated as a kind of organic B horizon in the relatively impermeable fine-textured sedimentary layers. There is no additional evidence for soil formation during the accumulation of the organic layers, however, e.g. no podzolized horizons or illuvial iron-oxide horizons. The iron bands that do exist can be explained by fluctuations in the water table through sediments of differential permeability. The writers therefore favor the

first view, that the black layers are of sedimentary origin and the organic material contained within them was not introduced later from above.

The "upland" just north of the swamp is exposed to a depth of about 4 m in the ditch. The material consists of a medium- to coarse-grained sand, locally cross-bedded and containing lenses of grit and some scattered pebbles. A few clay laminae may be traced into the upland area from the peat site. The sediment is interpreted as dominantly glacio-fluvial, with perhaps some eolian sand in the upper part. The involution layer so conspicuous near the peat site is traceable up the flank of the "upland" but is shallower and thinner. It is absent completely on the upland itself, as is also the capping peaty turf. Both of these features are thus confined to the lower regions of greater soil moisture.

PALEOBOTANICAL EVIDENCES OF VEGETATION, CLIMATE, AND AGE

RADIOCARBON DATES

In order to get an idea of the type of vegetation and climate during the transition from the Mankato to the Two Creeks interval, the buried peat and the overlying sand layers were subjected to macrofossil and microfossil (mainly pollen) analyses. In addition, the black involution layers were examined for their pollen content.

Macrofossils.—A collection of macrofossils from the buried peat was examined in 1957 by J. W. Moore, Dept. of Botany, University of Minnesota, who found the following plant species: *Picea glauca* (seed), *Sparganium minimum*, *Potamogeton foliosus*, *P. robinsii*, *P. zosteriformis*, *Najas flexilis*, *Carex cryptolepis*, *C. vesicaria*, *Hippuris vulgaris*, *Myriophyllum exallescens*, and *Menyanthes trifoliata*.

For additional information on the macrofossil content of the peat and the sand just below and above, pieces 10 by 10 by 4 cm in size were cut out and treated with HNO₃ diluted to about 1:4, washed, and sieved through a fine gauze sieve of 0.4 mm² mesh size.

One large piece of wood was identified microscopically by the Forest Products Laboratory (U. S. Dept. Agriculture), Madison, Wisconsin, as *Larix laricina*. Probably there is also some wood of spruce, here likely black spruce (*Picea mariana*). This identification has not been verified by microscopic study, but the pollen spectra show a great amount of spruce pollen (see below).

The peat, 10 to 15 cm thick at the sampling site, consists mainly of mosses, especially in the upper half. Among the mosses *Calliergon Richardsoni* (Mitt.) Kindb. is the most common, followed by *Drepanocladus aduncus* (Hedw.) Warnst. (determined by O. Mårtensson, University of Uppsala, and H. Persson, Natural History Museum, Stockholm). They have on the whole a northern distribution (Grout, 1931, p. 96, 108). *D. aduncus* has been identified from the Two Creeks forest bed, Wisconsin by Cheney (1930, 1931) but not by Culberson (1955). Neither species was reported among the mosses at the Loring Park site, Minneapolis, Minnesota (Cooper and Foot, 1932), which is probably of Two Creeks age or slightly younger (Wright and Rubin, 1956).

The macroscopic plant remains in the peat, identified by Fries, are the following (in estimated frequencies):

Larix laricina, wood (one piece microscopically identified—see above), especially in the transition zone between the peat and the overlying sand, twigs with short spurs (rare), needles (common), cones (rare). Fig. 5a. Distribution map in Munns, 1938.

Cf. *Picea mariana*, seeds and seed wings (less common). Determination unsure; cross-sections of seeds show similarities to *Larix*, Fig. 5b. Map ibid.

Sparganium cf. *minimum*, fruits (rather common). Fig. 5f. Cf. fruits in Muenscher, 1944, p. 25; Gleason, 1952, p. 73; and Fassett, 1957, p. 52; map in Muenscher, 1944, p. 21.

Potamogeton cf. *alpinus* var. *tenuifolius* or var. *subellipticus*, fruits (common). Fig. 5c. Cf. fruits in Ogden, 1943, pl. 746; Gleason, 1952, p. 77; map in Ogden, 1943, p. 91.

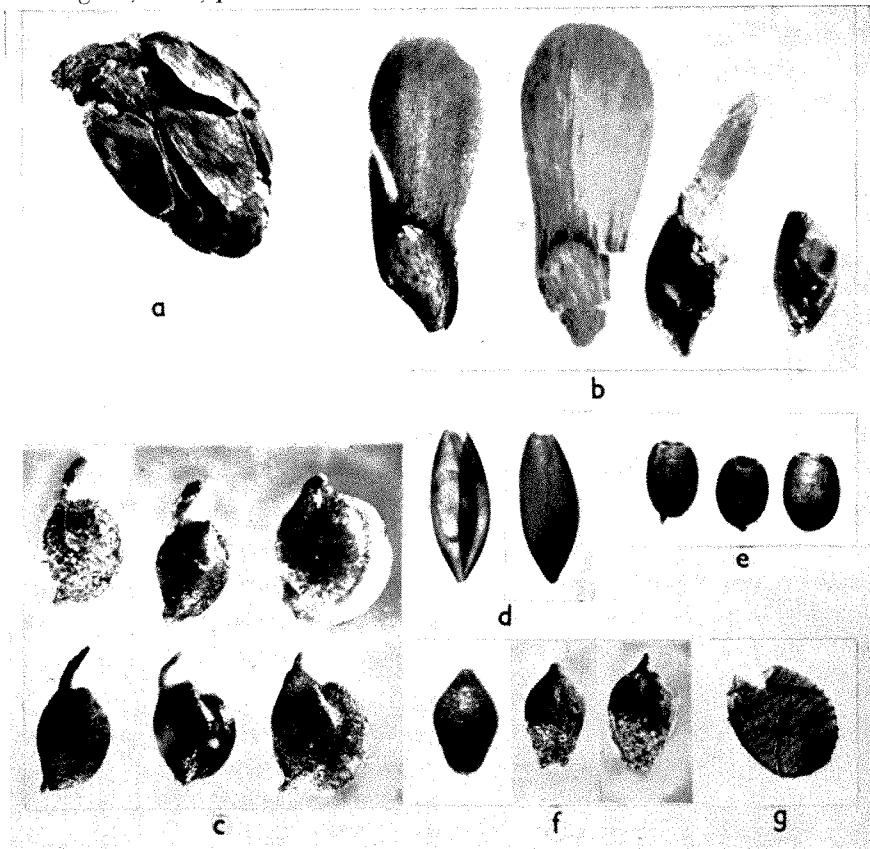


Fig. 5. Macrofossils identified from the buried peat in comparison with some modern forms. a. *Larix laricina*, cone. $2\frac{1}{2}X$. b. Cf. *Picea mariana*, from left to right: modern seed with wing, fossil wing, two fossil seeds, one with partial wing. Determination unsure; cross sections of seeds show similarities to *Larix*. $6X$. c. *Potamogeton* cf. *alpinus*, three fossil fruits (lower row) compared with three modern fruits of *P. alpinus* var. *tenuifolius* (upper row). The two fruits on the right with pericarp present. $6X$. d. *Najas flexilis*, fossil seeds. $6X$. e. *Hippuris vulgaris*, two fossil fruits (right) compared with one modern (left). $6X$. f. *Sparganium* cf. *minimum*, two fossil fruits (right) compared with one modern (left). $6X$. g. *Chara* sp., oosporangium. $30X$.

Potamogeton cf. *zosteriformis*, fruits (rare). Cf. fruits in Fernald, 1932, pl. 28; Muenscher, 1944, p. 49; and Gleason, 1952, p. 79; maps in Fernald, 1932, p. 37; and Muenscher, 1944, p. 56.

Najas flexilis, seeds (common). Fig. 5d. Cf. fruits in Muenscher, 1944, p. 70; and Gleason, 1952, p. 85; maps in Muenscher, 1944, p. 66, Dansereau, 1957, p. 33; and Hultén, 1958, p. 194.

Carex spp., fruits (rather common).

Hippuris vulgaris, fruits (less common). Fig. 5e. Cf. map in Muenscher, 1944, p. 277.

Myriophyllum exallescens, fruits (rare). Cf. map *ibid.*, p. 283.

Menyanthes trifoliata, seeds (rather common). Cf. map *ibid.*, p. 301.

Chara sp., oosporangia (common). Fig. 5g.

Mosses (see above).

Most of the fruits and seeds of the aquatic plants are more common in the lower half of the peat.

At present the species mentioned above show a distribution of more or less northern tendency. They all belong to the Boreal and the Great Lakes-St. Lawrence Forest regions north of the Deciduous Forest region (Rowe, 1959), even if some, as *Najas flexilis* (see above), are not confined to these regions.

Pollen.—The samples were prepared for pollen analysis with the use of hydrofluoric acid (in case of mineral material) and acetolysis solution according to the procedure summarized by Faegri and Iversen (1950, p. 58 ff.). The calculation of the percentages is based on the sum of arboreal pollen (Σ AP), cf. fig. 6.

The pollen spectra of the peat and the adjacent sand are characterized by high spruce-pollen values (fig. 6). The other tree-pollen types are of subordinate importance. Among these, however, oak and ash are rather prominent. The very low values of pine are worth observing. Also noted are some pollen grains of *Larix*, unexpectedly few in comparison with the macrofossils (cf. above), and some of *Thuja* or *Juniperus*. Of *Populus* very few pollen grains were observed.

Several nonarboreal pollen (NAP) types occur. Cyperaceae are strongly represented. Of special interest are the comparatively high values of *Artemisia* and of other Compositae pollen types (mostly *Ambrosia*). Also some pollen of Gramineae, Chenopodiaceae (or Amaranthaceae), Caryophyllaceae, and Cruciferae occur in small amounts. Only one pollen grain of Ericales type was observed. Eight pollen grains of *Elaeagnus commutata* were found in different layers of the peat.

Among pollen of water and swamp plants (except Cyperaceae) the following types occur in the peat, generally in low frequencies: *Typha latifolia*, *Sparganium* sp., *Potamogeton* sp., *Thalictrum* sp., *Myriophyllum* cf. *exallescens*, and *Menyanthes trifoliata*. Among the green algae some specimens of *Pediastrum boryanum* (Smith, 1920) were noticed in the samples, all of which were acetolyzed.

The interpretation of these pollen spectra is tentatively the following:

In the shallow basins there were swamps of different types as well as open water. There were sedge swamps with open, moss-covered patches, and tree-

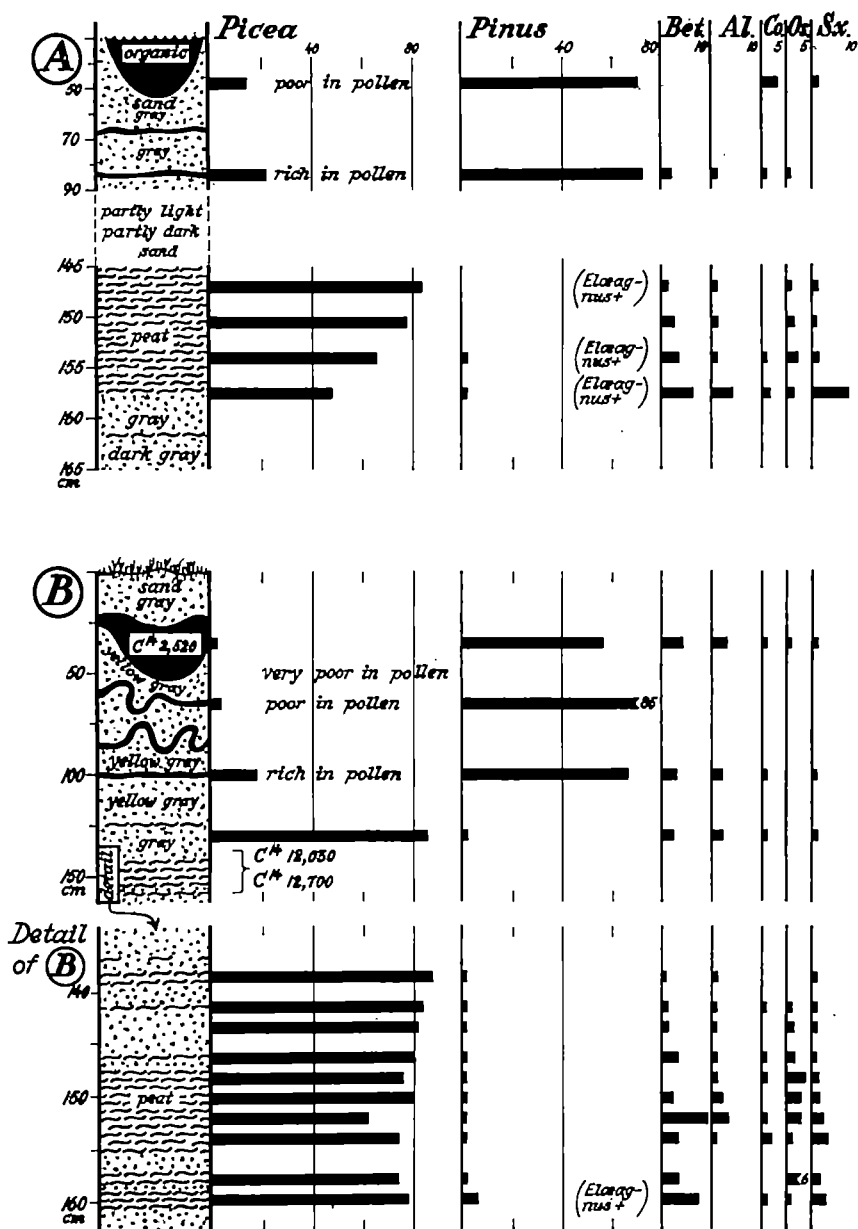
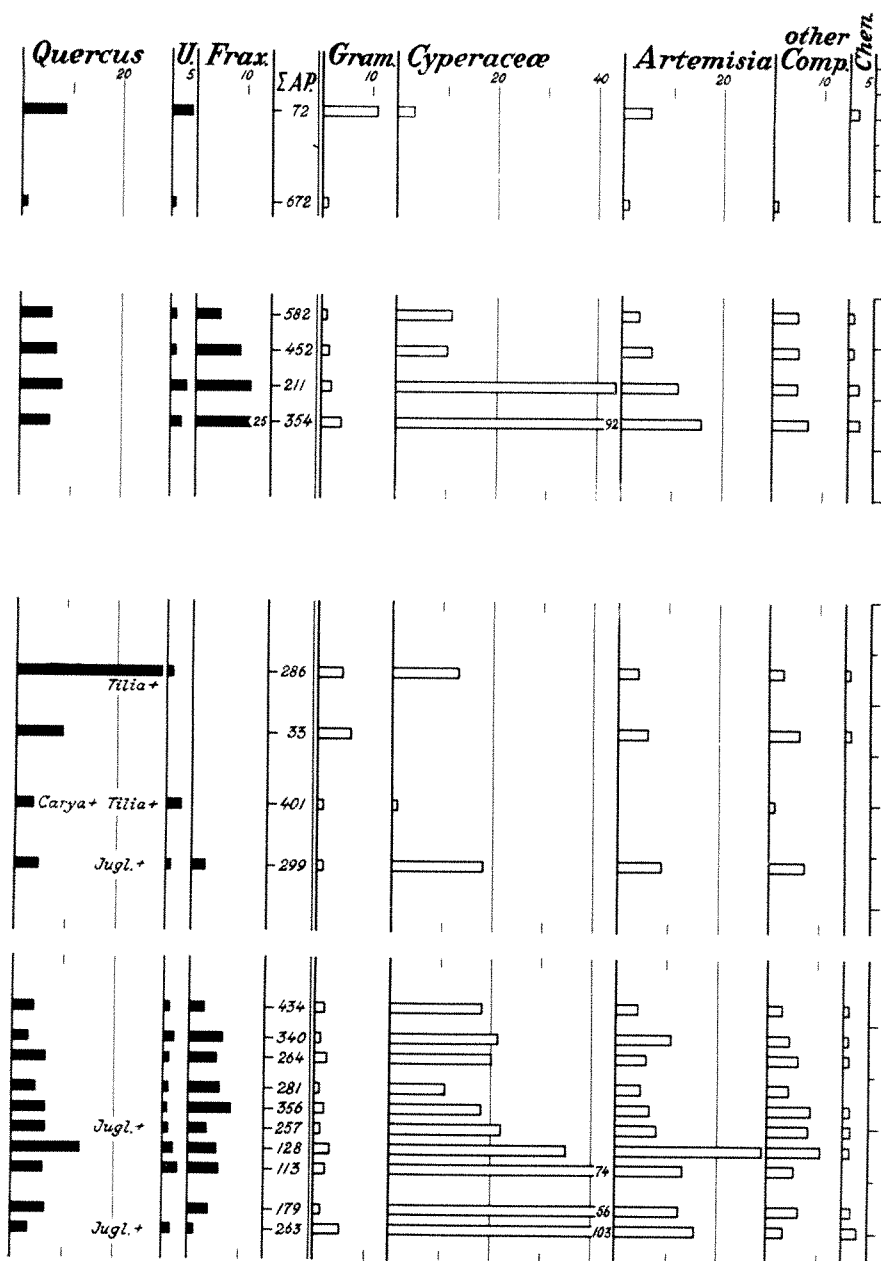


Fig. 6. Stratigraphic profiles and pollen spectra from North Branch site. Explanation: *Bet.* = *Betula*, *Al.* = *Alnus*, *Co.* = *Corylus*, *Os.* = *Ostrya* (or *Carpinus*), *Sx.* = *Salix*, *U.* = *Ulmus*, *Frax.* = *Fraxinus*, *Gram.* = Gramineae, other *Comp.* = Compositae except *Artemisia*, *Chen.* = Chenopodiaceae (or *Amaranthaceae*), Σ AP = sum of arboreal pollen.



covered swamps with at least tamarack (*Larix laricina*) and most probably also with black spruce (*Picea mariana*). Equivalent types of swamp occur today in the surroundings and toward the north and northwest, e.g. Cedar Creek Bog about 15 miles WSW of the North Branch site, and others described by Conway (1945). It is not certain that the *Picea* pollen represents only the black spruce of the swamps or if it includes pollen of the white spruce (*Picea glauca*) of the upland. It seems more reasonable to assume that most of the spruce-pollen grains were derived from local *Picea mariana* stands.

The relatively great amount of NAP indicates that the upland with the low hills of outwash sand or locally of till was not totally covered by forest. In addition to limited places with ephemeral vegetation of pioneer character on sand bars in the river floodplain, there seem to have been at least patches of open ground or a sort of parklike landscape with scattered trees or groups of trees. Regarding the frequency of NAP together with relatively high amount of *Quercus* pollen there may have existed a type of oak forest, similar to those on dry hill slopes in the area today, or a savanna vegetation with oak openings, typical for the prairie border (Curtis, 1959, p. 132 ff., 325 ff.). Thus *Quercus* species such as *alba*, *borealis*, *ellipsoidalis*, and *macrocarpa* may be considered. The NAP flora (*Artemisia*, *Ambrosia*, other composites, chenopod-amaranthus) indicates rather xerophytic vegetation on the open areas. This is especially pointed out by the occurrence of *Elaeagnus commutata*, a prairie shrub in western Minnesota, the Dakotas, and areas to the west. Pollen of this xerophytic shrub was found in late-glacial sediments in Michigan by Andersen (1954, p. 144 ff., pl. VIII). These finds in eastern Minnesota and in Michigan seem to indicate that there were prairie conditions at least locally during some part of the late-glacial time over areas where later in postglacial time forest covered the landscape.

The amount of pollen of *Quercus* sp. and *Fraxinus* sp. may be considered surprisingly high for late-glacial deposits. The possibility of occurrence of redeposited (secondary) pollen must be taken into consideration. Although it might be possible that laminated moss peat was formed in situ (the mixed-in sand may have blown out over the swamp surface from time to time), an allochthonous peat formation in water may well have occurred in a floodplain landscape like this (cf. the preceding pages). In any case, the peat-forming material, including the embedded macrofossils, must be of late Mankato or early Two Creeks age, whether it is transported some distance or not. The radiocarbon dates confirm this. The more important question, whether or not there are secondary microfossils washed into the peat, may still be open. It seems more plausible to assume that the pollen contribution from the Anoka sand itself, extremely poor in microfossils, was so minute that it could not make itself conspicuous among the probably rich local pollen precipitation at that time. Furthermore, the list of macrofossils indicates a comparably favorable climate (cf. the maps referred to in the macrofossil list above). Even if the possibility of redeposited pollen grains in the peat cannot be totally excluded, it is more likely that the spectra show the real situation at the time of the peat formation.

The macroscopic plant remains and the pollen spectra from the peat and the dark sand just below and above indicate:

(1) The chronological position in late-glacial time because of dominating *Picea* and high amount of NAP.

(2) Temperature conditions favorable to certain northern hardwoods, especially oak and ash species, and some water plants (e.g. *Najas flexilis*), indicating a temperature perhaps only slightly colder than today.

(3) Probably drier conditions than nowadays shown by a vegetation of more or less xerophytic and heliophilous character.

The black organic layers with involutions in the sand overlying the buried peat show an opposite type of pollen spectrum, characteristic of postglacial pollen zones. The most important feature here is the dominance of *Pinus* pollen. Also *Quercus* is well represented, especially in the thick, uppermost involution layer. *Picea* has minor importance.

Radiocarbon dates.—A date of $12,700 \pm 250$ B.P. (W-389) was obtained from a sample of the buried peat, and a date of $12,030 \pm 200$ B.P. (W-354) for a piece of wood taken from near the base of the peat (Wright and Rubin, 1956; Rubin and Alexander, 1958). The discrepancy between the two dates is not explained but is not considered to be of great significance.

A sample for radiocarbon dating was cut out of the big involution layer about half a meter below the soil surface (cf. fig. 4). The date obtained, 2520 ± 200 B.P. (W-872) (Rubin and Alexander, 1960, p. 150), confirms the postglacial age of this layer of black organic soil.

ORIGIN OF THE INVOLUTIONS

Involution of the type exposed at the North Branch site are generally attributed to the intense pressures developed during autumn near the base of the active layer of permafrost, as the water-saturated sediment is pressed between the downward-freezing crust of annual frost and the rigid base of permafrost (Steeger, 1944; Sharp, 1942). The features are also known as *Taschenboden*, *Würgeboden*, cryoturbations, and plications. They have also been termed *Brodelboden* with the implication that they are produced by convection of fine-grained sediment supersaturated with water during the time of temperature changes in the soil.

Involution is common in the periglacial region of Europe and have been used to indicate the distribution of permafrost during the last glacial period (Poser, 1948). They are not ordinarily found in deposits of the last glaciation, and it is therefore inferred that permafrost did not follow the retreating ice.

If the North Branch involutions require the presence of permafrost, then their occurrence in sediments younger than the late Mankato–Two Creeks buried peat implies the recurrence of low temperatures in a younger climatic phase, i.e. the Valdres, or at least the persistence of permafrost through the Two Creeks interval. The pollen analyses, however, show by their high percentages of pine relative to spruce that the involuted sediments were formed during the postglacial rather than late-glacial, and the radiocarbon date of 2520 B.P. confirms this postglacial age. The involutions therefore must have

been formed in very recent time, when there is no possibility of permanently frozen ground. The mean annual temperature of the area at the present time is about 6°C, and a mean temperature certainly below 0°C is a requisite for permafrost formation. Either the involutions are related to annual frost or were formed in some entirely different way.

The mechanism of formation of the European periglacial involutions has not been fully explained because few features of this type have been observed in the process of formation in present permafrost regions. Hopkins and Sigafoos (1951, p. 98) describe soil distortions that have resulted from frost-heaving of tussocks in western Alaska, and suggest that some "fossil" involutions may have formed in this manner. In another study, Sigafoos and Hopkins (1951) describe similar tussocks in a swamp in Massachusetts, where the winter temperatures are even warmer than in Minnesota at present. Although no involutions were described in the Massachusetts occurrence, the authors indicate that tussock formation under the influence of annual frost action causes intensive soil disturbance.

Involutions similar to those at the North Branch site were described from the deposit of Glacial Lake Agassiz in eastern North Dakota by Horberg (1951), who adduced them to support his hypothesis that a peculiar pattern of intersecting grooves on the lake floor represents former ice-wedge polygons in permafrost. Nikiforoff (see Horberg, 1951) points out, however, that the involutions could not have formed until after Lake Agassiz had been drained, long after the ice retreated from the Valders terminus. All pollen-analytical evidence presently being assembled in Minnesota indicates that the climate by this time was too warm for the persistence of permafrost at shallow depth. It may therefore be concluded that involutions are not necessarily a valid criterion for past permafrost.

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CHARACTERISTICS OF BEACHES FORMED IN POLAR CLIMATES

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ABSTRACT. Beaches formed in polar climates are characterized by features that generally are not found in beaches formed in nonpolar climates. Arctic and Antarctic beaches commonly show one or more of the following features: (1) They rest on ice. (2) They are pitted. (3) They have ridges and mounds formed because of ice push and/or deposition from stranded ice. Those formed by ice push are commonly associated with beach scars. (4) They have beach ridges that terminate abruptly because ice was present when they were formed. (5) Ice-rafted fragments are found on them. (6) They have poorly rounded beach stones. (7) Frost cracks and mounds, stone circles and polygons, and solifluction deposits are found on them. (8) They are associated with striations formed by sea ice and icebergs. (9) The beach ridges may have short erosional gaps that were formed by meltwater streams. (10) The beaches are associated with ice-contact features (proglacial deltas, eskerlike features) and glaciomarine deposits. (11) Ventifacts are present. (12) They contain cold-water fossils. (13) They may contain the soft parts of marine organisms.

Ancient beaches that have one or more of these characteristics may have formed in a polar climate.

INTRODUCTION

Ridges, swales, cusps, wave deltas, and other features are found on beaches formed in both nonpolar and polar climates. However, beaches formed in polar climates have certain characteristic features which formed because of the presence of permafrost and land and sea ice. "Polar climates" is not used in a strict climatological sense in this paper. It includes the tundra, ice-cap, subarctic, and even highland climates of Finch and Trewartha (1936, p. 245-270), as well as the climates of those regions where there is or has been abundant sea ice, lake ice, water-terminating glaciers, or deeply frozen ground.

ACKNOWLEDGMENTS

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BEACHES RESTING ON ICE

Most and perhaps all of the active part as well as the inactive and slightly elevated part of a beach approximately 2000 feet in length a few miles north of Marble Point between the Wright Glacier and Gneiss Point, McMurdo Sound, Antarctica is resting on ice (fig. 1; pls. 1-A, 2-A). The gravel blanket-
ing the ice is in places several feet thick. Two to three feet of gravel is interbedded with the ice (fig. 2). In places the gravel blanket is thinner than the

unlikely that the deposition of a layer of gravel of varying thickness on either a regular or irregular pre-beach surface would produce a smooth surface. The trenches are about at right angles to the elongation of the beach. One was 50 feet long, 18 feet wide, and 3 to 6 feet deep. Outlet streams from the small ponds behind the beach frequently run across the beach, as indicated by the thin, fine-grained fluvial deposits in some of the trenches. The streams are not strong enough, however, to form trenches in the beach by removing beach gravel. However, the pond water at times is undoubtedly above 32°F, and it seems likely that the outlet streams have melted the ice immediately beneath the gravels and in this way formed the trenches.

Pits, hollows, hillocks, and mounds are found on the beach at Marble Point, which rests on several feet of clean ice. The area containing the pits is about 1500 feet long and 200 to 400 feet wide. It is in most places between 45 and 55 feet above sealevel, and it contains hundreds of pits (pl. 2-B). The pits are round, oblong, or irregular (pl. 1-B). Most are single, but two or more may coalesce. The single pits range in diameter from 13 to 40 feet. One oblong compound pit is 115 feet long. Most of the pits are less than 4 feet deep, although some are as much as 6 feet deep. Most are dry, but during the summer a few contain water, which comes from the melting of the ice. These pits, like those on the pitted beach between the Wright Glacier and Gneiss Point, were formed by the differential melting of the ice beneath the beach gravels.

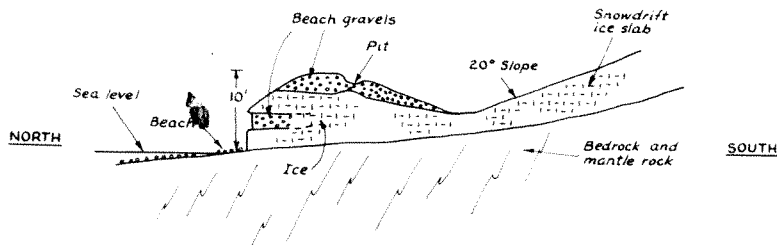
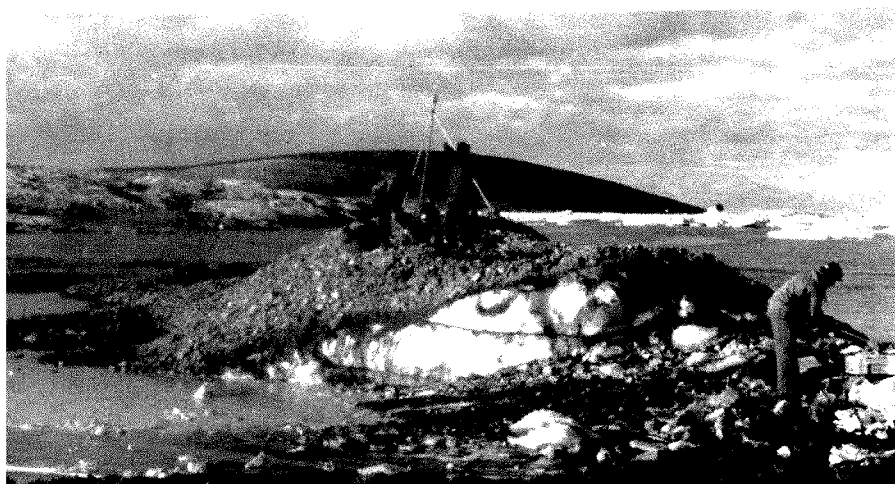


Fig. 2. A diagrammatic sketch showing the relationship of the beach to the ice foot.

If an ancient beach that rests on ice is not pitted, the active layer since the formation of the beach has never been as thick as the beach gravels. If the gravels of a pitted beach that rests on ice are thicker than the present active layer, the beach has probably been in existence during a warmer climate than that at present.

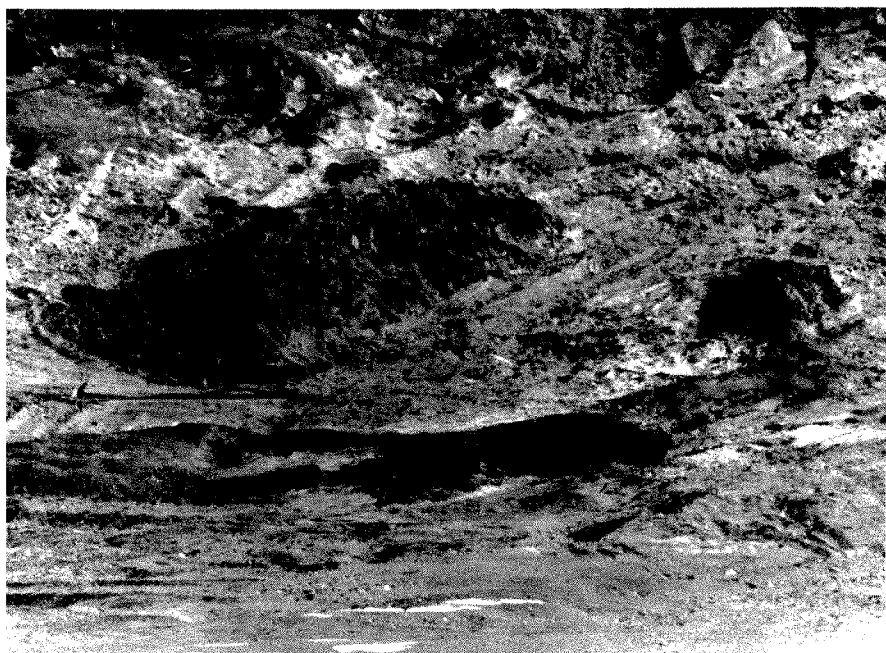
The U. S. Navy, in carrying out engineering studies, removed with a bulldozer between 1 and 2 feet of sand and gravel from a part of the elevated pitted beach. A few weeks later, collapse depressions developed in the sands and gravels because ice beneath them melted, and well-developed thermokarst topography (Péwé, 1954, p. 329-338) was formed. The removal of the gravel by bulldozing brought the ice well within the active zone. One depression was 13 feet long, 9 feet wide, and 15 inches deep (pl. 3-B). Some of the depressions contained water from the melting ice; others had damp sand at the bottom. The ice was in most places only a few inches below the bottom of the depressions. Ridges of sand and gravel with medial tension cracks as well as mounds with radial tension cracks also formed because of differential collapse.

PLATE 3-A



An ice-cored gravel ridge approximately 120 feet long and more than 9 feet high surrounded by sea ice and located about 100 feet offshore near Marble Point, McMurdo Sound, Antarctica. The core of ice, the veneer of gravel, and two layers of interbedded sand are shown.

PLATE 3-B



Collapse depressions in beach gravel at Marble Point, McMurdo Sound, Antarctica, resulting from the differential melting of ice beneath the gravel following the removal of a few feet of gravel by bulldozing. Same area as that outlined by white ink on plate 2-B.

This pitted beach resembles pitted outwash, but the material in the pitted beach is much better sorted than the outwash deposits in the Marble Point area. The pitted area is immediately below higher elevated beaches, whereas pitted outwash is usually found above the marine limit. Also, the bifurcation of the mainland side of the pitted area (pl. 2-B) would be expectable if the area were an elevated pitted beach, but would not be expectable if the pitted area were outwash.

Pitted beaches are formed not only by the burial of an ice foot and growlers, floes, and small blocks of ice by beach deposits, but also by the burial of the snout termini of glaciers. The Wilson Piedmont Glacier nearly reaches the strandline for a distance of approximately 400 yards immediately south of the deglaciated mainland near Spike Cape about 10 miles north of Marble Point, McMurdo Sound. A gravel ridge about 400 yards long, up to 7 feet high, and in most places less than 30 feet wide is found between the ocean and the terminus of the glacier. Although the ridge is more or less continuous, it has gaps that are scores of feet long. In other places small isolated gravel hillocks as much as 4 feet high take the place of the ridge. Pits and mounds are found on the ridge. The gravel is unweathered and somewhat sorted, and the fragments are somewhat rounded. The similarity of this gravel to that found in the nearby beaches and the absence of morainal material on the nearby glacier prove that the gravel is a beach deposit and not morainal material. It is generally only a few feet thick and rests on ice. The nearness of the glacier indicates that the ice is a stagnant piece of glacial ice. The thickness of the up-turned floes immediately offshore indicates a steep offshore profile. The steep offshore profile and the snout terminus of the glacier enabled the waves to throw beach gravel derived from glacial deposits onto the foot of the glacier. Following the deposition of the gravels a small amount of glacial retreat took place. The gravels protected the ice beneath them, and an ice-cored gravel ridge with pits and hillocks was formed.

Pitted beaches indicate that land and/or sea ice or perhaps permafrost was present when the beaches were formed and are therefore diagnostic of polar climates. Some of the ancient beaches in New England, Scandinavia, the Great Lakes region, and elsewhere are probably pitted.

ICE-PUSHED AND ICE-DEPOSITED RIDGES

Marine ice-pushed ridges and mounds formed by sea ice, growlers, and bergy bits are found on beaches formed in polar climates. The material in the ridges and mounds is derived from the beach scars that are associated with them. Ice-pushed ridges and mounds are common on both the modern and elevated Arctic beaches (Washburn, 1947, p. 78-80; Nichols, 1953b), and the writer has seen them in the Antarctic.

Somewhat similar ridges and mounds are formed by the deposition of material from ice stranded on polar beaches. A gravel ridge approximately 120 feet long and projecting as much as 9 feet above sealevel was seen about 100 feet offshore near Marble Point. The sides in places slope at approximately 30°, but in most places they are gentler. The ridge is surrounded by water during a part of the summer and by sea ice during the remainder of the year

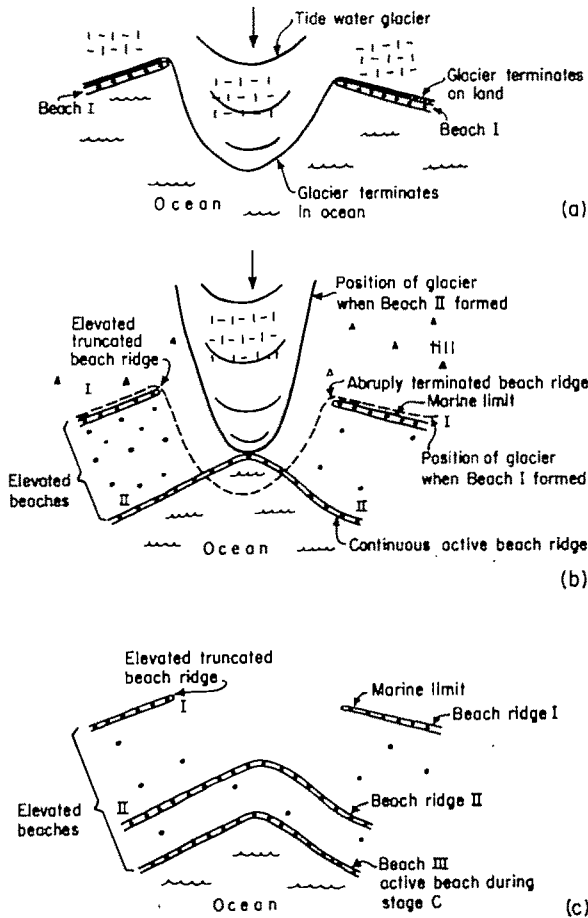


Fig. 3. Diagrams showing the formation of elevated beach ridges which terminate abruptly because of the former presence of glacial ice.

(pl. 3-A). A bulldozer cut made at the end of the ridge showed that the ridge had a core of ice and was only veneered with gravel. The gravel, on the average, was between 1 and 2 feet thick; the degree of rounding of the fragments and the gray color indicate that it is modern beach gravel. Interbedded in the ice were two thin layers of sand (pl. 3-A). The bottom of the ice was not seen, and other layers may be present. This ice mass is probably a detached, rafted, and stranded ice foot. The interbedded sand suggests that it may have been more than one year in forming. The active layer in this area, in gravels similar to those on this ridge, is 2 or more feet deep. The ice core is, therefore, slowly melting. When it has melted away, only a small ridge of gravel will remain, which will probably not be associated with a beach scar. Gravel ridges and mounds formed in this way are also found on nearby elevated beaches. Many others were probably destroyed by wave action.

Ridges and mounds composed of talus, landslide, fluvial, eolian, and solifluction material can also be formed in polar climates, as these types of de-

posits may collect at times on an ice foot (Brown, 1887, p. 358). It may not always be easy to differentiate a ridge or mound formed by ice push from one formed by deposition from an ice foot or from floating ice of other origin. However, those ridges and mounds that are not associated with beach scars or are not composed of beach deposits are probably not due to ice push. As the small masses of ice responsible for these features cannot be drifted very far into warm waters, the presence of either type of ridge on an ancient beach in general indicates that the beach was formed in a polar climate as defined in this paper.

Depressions and hollows that do not have ridges or mounds associated with them are found on polar beaches (Nichols, 1953c, p. 61). The absence of ridges and mounds and the presence of normal beach faces both above and below these depressions and hollows suggest that gravel may have been removed from the beaches. Joyce (1950, p. 646) has noted that an ice foot becomes on disintegration a powerful transportation agent as beach material frozen to

PLATE 4



A beach which terminates abruptly in the distance against a thick and high snowdrift ice slab.

the underside is rafted away. Many scars were probably formed in this way. Scars formed in this way are found only on polar beaches, as the ice foot is not developed in nonpolar climates.

TRUNCATED BEACHES

Some beaches terminate abruptly against cliffs, knobs, and upland areas; others end in deep water. Once-continuous elevated beaches may stop abruptly because they have been in part destroyed by fluvial or glacial erosion or because of burial by talus, landslide, solifluction, or eolian deposits. Beaches that are continuous for long distances and that terminate abruptly against glaciers or snowdrift ice slabs are common in the Antarctic (pl. 4). If, following the formation of such a beach, glacial retreat and uplift consequent on deglaciation take place, an elevated beach that terminates abruptly will be formed (fig. 3). These are also found in Antarctica. In most cases it should be easy to distinguish between abrupt truncation resulting from the former presence of ice and abrupt truncation resulting from other causes. If the highest beach ridge terminates abruptly and is pitted, it seems likely that not only the pits but also the abrupt termination of the beach are due to the presence of ice when the beach was formed.

PRESENCE OF ICE-RAFTED FRAGMENTS

Ice-rafted fragments are found on modern and elevated beaches in the Arctic, the Antarctic, and elsewhere (Washburn, 1947, p. 80-82; Coleman, 1922, p. 11-12). The ice-rafted origin of a fragment is fairly certain if all of the following conditions are met: (1) the fragment is much larger than the largest roundstones on the beach that have been transported and deposited by waves and shore currents; (2) it rests on the beach deposits and does not project through them from till or other deposits below; (3) the beach has not been over-run by glacial ice; (4) the fragment is angular or subangular and striated; (5) similar fragments are found up to the marine limit but not above it; (6) it is lithologically unlike the local till or bedrock. Ice-rafted fragments can be deposited on beaches formed in nonpolar climates. However, if the ice-rafted fragments are both large and numerous, the beach was probably formed in a polar climate. In some cases it might be difficult to differentiate fragments transported in the roots of trees and in other special ways from ice-rafted fragments.

DEGREE OF ROUNDING OF BEACH STONES

The gravel on many of the Antarctic beaches is as well rounded as that on the beaches in nonpolar climates. However, the degree of rounding of the fragments on some of the Antarctic beaches studied by the writer contrasts markedly to that occurring on beaches formed in nonpolar climates. The fragments on these Antarctic beaches in general have been only slightly rounded on the edges and corners by wave action. This poor degree of rounding is surely not due to lithologic types peculiar to Antarctic beaches, which are difficult to round. It is probably due to the short season during which there was open water, to the presence of an ice foot and/or stranded pieces of ice on the beaches when there was open water in the past, perhaps to an ice veneer on some of the beach stones for part of the time when there was open water

(Wright and Priestley, 1922, p. 311-312; pl. 214), which protected the beach stones from rounding, and to the rapidity with which the land has risen.

FROST FORMS

Frost cracks, some of which are hundreds of feet long, several feet wide, and a few feet deep, are common on Arctic elevated beaches (Washburn, 1947, p. 102; Nichols, 1953a, p. 271, 275). The furrows are commonly margined by levees, and they outline polygons which may be more than 100 feet in diameter. They are found in many kinds of mantle-rock deposits and are almost invariably underlain by wedges of ice. Similar furrows, also outlining polygons, are found on the elevated beaches near Marble Point, Gneiss Point, and elsewhere in McMurdo Sound, Antarctica. Péwé (1959) has shown that sand wedges rather than ice wedges underlie some of these Antarctic furrows. It seems likely that both the ice-wedge and sand-wedge polygons characterize beaches formed in polar climates.

Stone polygons and circles are also found on Arctic elevated beaches (Nichols, 1953a, p. 271, 275). Frost mounds are very common in the swales of the elevated beaches at Resolute Bay, Cornwallis Island, Northwest Territories, Canada. They are from 1 to more than 3 feet in diameter and are several inches high.

As solifluction is a common process in polar climates it is not surprising that elevated beaches in both the Arctic and the Antarctic are in places overrun and buried by solifluction sheets and lobes. Solifluction sheets bury some of the elevated beaches on Victoria Island, Northwest Territories, Canada, and at Thule, Greenland (Washburn, 1947, pl. 23; Nichols, 1953a, p. 271-272). Elevated beaches at Cape Bernacchi, between Spike Cape and the Wright Glacier, and elsewhere in McMurdo Sound, Antarctica, are now being progressively buried by solifluction sheets (fig. 1). Beaches now in nonpolar climates that are characterized by fossil frost cracks, stone circles and polygons, frost mounds, and associated solifluction features formed contemporaneously with the beaches, were formed in polar climates.

STRIATIONS

Sea ice and icebergs can striate bedrock (Gould, 1928, p. 37; O'Neill, 1924, p. 34A; Mathiassen, 1933, p. 32, 69, 94). The process in general operates in polar climates, where the ice is thicker and more abundant than in more temperate climates. The following criteria can be used to differentiate these striations from glacial striations: (1) they are not associated with well-planed and smoothed outcrops; (2) in general they are not so deep, straight, or long as are glacial striations; (3) they are oriented in general at high angles to the strandline; (4) chatter marks, grooves, trenches, and roches moutonnées are absent; (5) short cross striae are probably more commonly formed by sea ice and icebergs; (6) they are not well developed on vertical and steeply inclined surfaces.

The striations formed by sea ice or icebergs are not found, of course, much above the marine limit. If bedrock outcrops associated with raised beaches now found in nonpolar climates show striations similar to those formed

by sea ice and/or icebergs, there is justification for assuming that these beaches may have been formed in a polar climate.

Beach gravels may be striated by ice thrust up onto the beach (Leffingwell, 1919, p. 174). However, fragments striated in this way are rare, and the striations are faint. It might be difficult to differentiate striated fragments deposited on beaches by icebergs from those formed in this way. In either case, the presence of striated fragments on a beach suggests that the beach was formed in a polar climate.

CAPS IN BEACH RIDGES FORMED BY MELTWATER STREAMS

A gap approximately 100 feet long is found in the highest beach ridge not far from Marble Point, McMurdo Sound, Antarctica. The beach ridges immediately below it are, however, continuous. The gap was probably eroded by a meltwater stream from the nearby Wilson Piedmont Glacier. The absence of gaps in the lower beach ridges indicates that the meltwater stream, probably because of glacial retreat, was no longer active in this area when the lower beach ridges were formed.

ASSOCIATION WITH ICE-CONTACT FEATURES AND GLACIOMARINE DEPOSITS

Crosby and Lougee (1934, p. 447), Trefethen and Harris (1940), Flint (1947, p. 142), and others have described proglacial deltas and eskerlike features built against ice that terminated in the ocean. Ancient beaches formed in polar climates may be associated with these features. Beaches whose distribution, elevation, and degree of weathering prove that they were formed at the same time as these features, originated in a polar climate.

The glaciomarine sediments formed in the vicinity of a glacier that terminates in deep water are characterized by distinctive features. They may be interbedded with glaciomarine sediments if the terminus of the glacier fluctuated during the deposition of the marine sediments. Ice-rafted stones, particularly of local origin, may be abundant in glaciomarine sediments. Contemporaneous deformation in glaciomarine deposits due to glacial shove and to the drag of icebergs on the bottom should be common; so too should cold-water fossils. Many ancient beaches contemporaneous and close to this kind of glaciomarine deposit were probably formed in a polar climate.

VENTIFACTS

Ventifacts are found on a few of the higher elevated beach ridges near Marble Point. They are highly polished, and the cutting in general has removed less than one quarter of an inch of rock. They were formed by winds from the south, as only the southern sides in general are cut and polished. Although little is known about the climate of the area, it seems certain that the ventifacts were developed during the cold season, as observations by the writer during three summer field seasons indicate that the winds are not strong during the warm season. The fact that the cutting was done during the cold season when the temperatures may be lower than minus 60°F (Simpson, 1923, p. 40) suggests that some of the polishing and cutting may be due to windblown snow and ice (Teichert, 1939; Blackwelder, 1940). The following factors favored their formation: (1) There has been no vegetation in the area since

POLYMORPHISM AND SUBSOLIDUS EQUILIBRIA IN THE SYSTEM $\text{GeO}_2\text{-TiO}_2^*$

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ABSTRACT. Evidence is presented for a metastable alpha- to beta-quartz transition in germania. The temperature of the stable inversion of the rutile to quartz form of GeO_2 is lowered by TiO_2 in solid solution. The maximum solid solubility of TiO_2 in the rutile form of GeO_2 is about 25 mole percent at $1023^\circ\text{C} \pm 5^\circ\text{C}$. The solubility in the quartz form is about 30 mole percent at 1050°C . The solid solubility of GeO_2 in TiO_2 is about 40 mole percent at 1050°C .

INTRODUCTION

Germania is interesting crystal-chemically in that it occurs in two well-established crystalline modifications in which the Ge^{4+} ion occurs in either tetrahedral or octahedral oxygen coordination. The Goldschmidt radius for the Ge^{4+} ion (0.53Å) lies between the radii of Si^{4+} (0.39Å) and Ti^{4+} (0.64Å). As ionic size is the most important factor in the determination of the type of lattice in which a particular compound will crystallize, it is not surprising that germania occurs in two forms analogous to stable polymorphs of silica and titania. The Ti^{4+} ion in oxides occurs almost invariably in 6-fold coordination, whereas the Si^{4+} ion prefers 4-fold coordination. The stable low-temperature form of GeO_2 has the rutile structure, whereas the high-temperature form has the quartz structure.

A detailed investigation of the polymorphism of GeO_2 was carried out by Laubengayer and Morton (1932). To establish the temperature of the rutile to quartz inversion with a reasonable degree of accuracy, they found it necessary to use a mineralizer, the most effective one being an addition of about 1 percent by weight of the eutectic mixture of LiCl-KCl . They found that the stable low-temperature rutile form changed slowly to the stable high-temperature quartz form at about $1033 \pm 10^\circ\text{C}$. The quartz form¹ was retained to room temperature quite readily. The stable melting point of GeO_2 was placed at $1116^\circ\text{C} \pm 4^\circ$, and the rutile form was found to melt metastably at $1086^\circ\text{C} \pm 5^\circ$.

Shafer and Roy (1956) determined the phase relations in the system $\text{SiO}_2\text{-GeO}_2$ as shown in figure 1. They found what appeared to be a complete series of β -quartz solid solutions although no β -quartz form of germania had ever been reported. It is very difficult to distinguish between the two forms of quartz by X-ray diffraction powder methods, so that, in the high GeO_2 portion of this system, the authors were never certain whether they were observing metastable β -quartz solid solutions or metastable α -quartz solid solutions at room temperature. Small additions of GeO_2 in solid solution in SiO_2 diminished the heat effect of the quartz inversion to practically zero. Differential thermal analysis and high-temperature X-ray diffraction experiments up to 700°C in-

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¹ Commercial germania is generally obtained as the quartz modification.

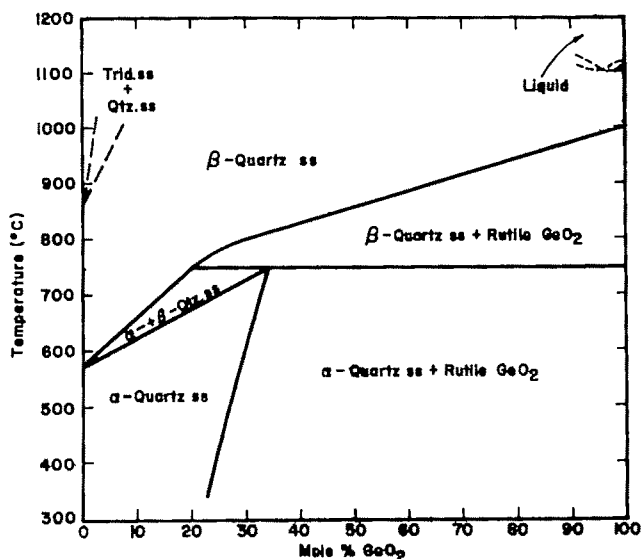


Fig. 1. The system SiO_2 - GeO_2 (Shafer and Roy).

dicated no inversion in the quartz form of germania. A chalcedonic-like variety of germania was recently prepared by White, Shaw, and Corwin (1958).

EXPERIMENTAL

Compositions were prepared on a mole percent basis at 10 percent intervals. TiO_2 (anatase) and the quartz form of GeO_2 were used as the starting materials. Because of the extreme sluggishness of reactions in this system in the temperature range studied, 800°-1050°C, 1 percent by weight of the eutectic mixture of LiCl-KCl was added to the batches in the form of an aqueous solution. At the maximum temperatures encountered in this work there should be no appreciable loss of either KCl or LiCl. KCl melts at 768°C and boils at 1411°C. LiCl melts at 606°C and boils at 1382°C. Although the melting temperatures are lowered owing to the eutectic relation, both the liquid and vapor phases should be completely miscible in all proportions, so that a simple ascendant t-x relationship should exist between the liquid and vapor regions in the p-t-x diagram for LiCl-KCl. This would indicate that there should be but negligible chloride volatilization at temperatures below 1050°C. The materials were mixed in a glass mortar for 15 minutes, dried, remixed for 15 minutes in acetone, and heated at about 750°C for 24 hours in platinum crucibles. The calcined material was remixed for 30 minutes in acetone in an automatic agate mortar and pestle and dried. The batches prepared in this manner were used as starting materials for the quench experiments. Glasses could not be prepared from compositions containing as little as 5 percent TiO_2 . Air-quenched melts in the high-germania portion of the system contained crystals of TiO_2 solid solutions. Even if glasses could be prepared, compositional changes due to GeO_2 loss would be excessive and probably would lead to inhomogeneous glasses.

For the determination of temperature-composition relations in the $\text{GeO}_2\text{-TiO}_2$ system, the conventional quench technique was used; small samples of material were held at constant temperature ($\pm 2^\circ\text{C}$) to attain equilibrium. The samples used for measurement of lattice parameters were sealed in platinum tubes to prevent GeO_2 loss. Others were packed into small unsealed platinum envelopes. Equilibrium phase assemblages were determined using a Norelco X-ray diffractometer with nickel-filtered $\text{CuK}\alpha$ radiation. Lattice parameters of solid solutions were determined and used for the fixing of phase boundaries. The accurate determination of these parameters was accomplished by using an internal standard of silicon for calibration and $\text{K}\alpha_1$ reflections which could easily be separated from $\text{K}\alpha_2$ reflections at high angles ($2\theta > 40^\circ$).

Differential thermal analysis apparatus was used to study the behavior of the quartz form of GeO_2 . The furnace was platinum wound and an average temperature rise of about $8^\circ\text{C}/\text{min}$ was controlled by a motor-driven variac. Heat effects were recorded on a General Electric X-Y recorder. Because of a temperature gradient along the axis of the furnace, differences in thermal conductivity between unknown and standard, and rapid heating rate, and because the temperature-measuring thermocouple was placed between the unknown and

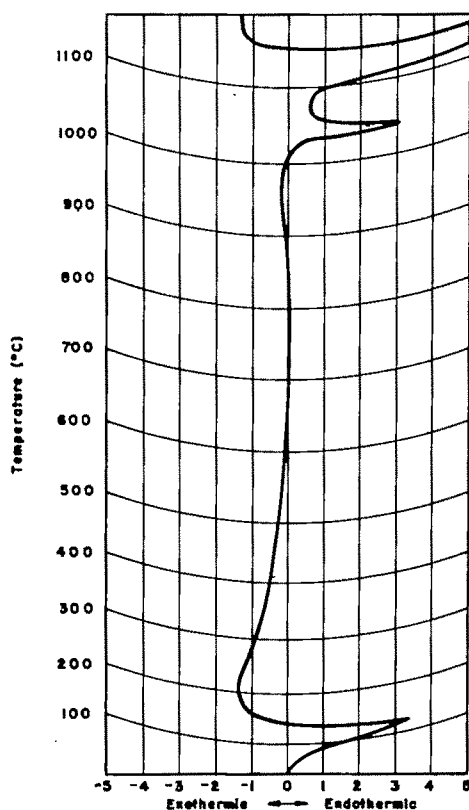


Fig. 2. Differential thermal analysis curve for GeO_2 quartz.

the standard along the length of the furnace, temperature readings may be in error to no more than 20°C of the actual temperature at the position of the unknown.

A high-temperature X-ray furnace mounted on the Norelco diffractometer was used for the determination of the axial thermal expansion coefficients of the quartz form of GeO_2 . At elevated temperatures, the variation in temperature could be held to less than one degree for any desired length of time.

An aggregate thermal expansion measurement of the quartz form was made using a bar of sintered material approximately 10 cm in length. The expansion was measured with a dilatometer calibrated in 0.0001-in. divisions. The rate of temperature rise in the apparatus was about 2°C/min from room temperature to 950°C.

RESULTS AND DISCUSSION

GeO_2 polymorphism.—One of the requirements for the formation of a complete series of solid or crystalline solutions between two compounds is that they must be isotypic. If the proposed system for SiO_2 - GeO_2 is correct, in which a complete series of β -quartz solid solutions is indicated, GeO_2 must also have a β -quartz structure in addition to the two previously established polymorpha, rutile and α -quartz. The commercial quartz variety has been shown to have the α -quartz structure which is hexagonal.

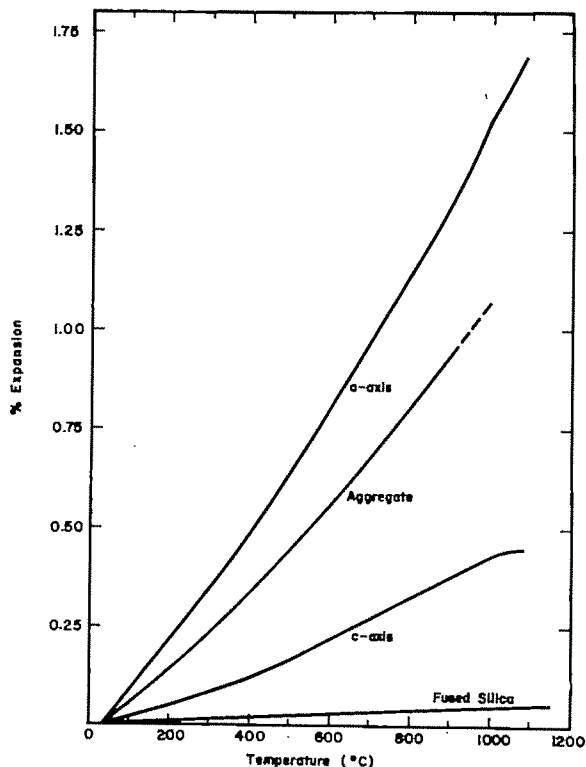


Fig. 3. Axial and aggregate thermal expansion curves for GeO_2 quartz.

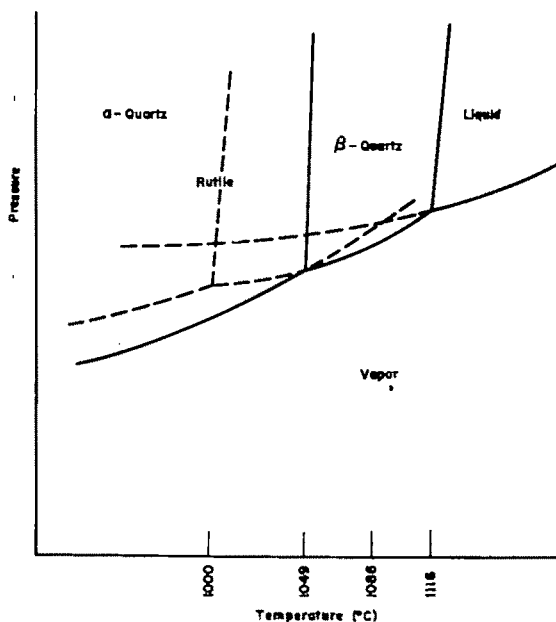


Fig. 4. Schematic P-T diagram for the system GeO_2 .

A sample of the quartz form was used for a DTA experiment, using Al_2O_3 as the inert standard. A drop of water was added to the GeO_2 as an indicator of proper functioning of the recording system at the start of the run. Figure 2 is a reproduction of the experimental curve obtained. The low-temperature endothermic peak is due to the volatilization of the water. No further heat effects occur until about $1000^\circ\text{C} \pm 20^\circ$, where a sharp endothermic reaction begins, followed by a much larger endothermic heat effect at about 1100°C . The peak at 1000°C is attributed to an inversion in the quartz form, whereas the peak at 1100°C is due to melting of GeO_2 . A second DTA experiment was carried out in which the quartz form was heated to a temperature between the inversion and melting temperatures. On cooling, an exothermic peak was recorded that was very similar to the endothermic peak obtained in the heating cycle. The only phase observed at room temperature was the quartz form. The possibility of a quartz to rutile inversion is ruled out because of the sluggish nature of this inversion, and because high-temperature X-ray diffraction experiments indicated only the presence of the quartz form up to 1075°C . In the absence of a mineralizer or high pressures, many hours at temperatures slightly below the rutile to quartz inversion are required to produce a trace of the rutile form from the quartz form.

Quenching experiments using a mixture of the quartz form of GeO_2 and 1 percent by weight of the LiCl-KCl mixture as a catalyst were carried out to fix the temperature of the stable rutile to quartz inversion. Small unsealed platinum envelopes containing this mixture were suspended in the quench furnace, and the results of these experiments are given in table 1. This tem-

perature was determined to be $1049^{\circ}\text{C} \pm 5^{\circ}\text{C}$ as compared to Laubengayer and Morton's (1932) value of $1033^{\circ}\text{C} \pm 10^{\circ}$.

TABLE 1
Quench data for rutile to quartz inversion in GeO_2

Temperature ($^{\circ}\text{C}$)	Time (hr)	Phase Analysis
1018	16	Rutile
1039	24	Rutile
1046	8	Rutile
1052	24	Quartz
1108	16	Quartz

The thermal expansions along the a- and c-axial directions of GeO_2 quartz as calculated from X-ray diffraction data are shown in figure 3. The aggregate expansion as measured by the dilatometer method is seen to fall between the axial expansions. The possible detrimental effect of sintering on the accuracy of the X-ray measurements was avoided by first sintering the

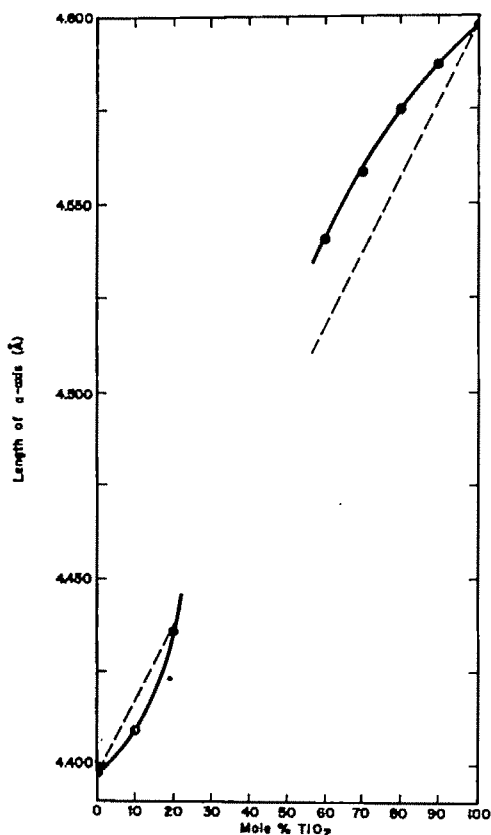


Fig. 5. Length of a-axis for rutile solid solutions.

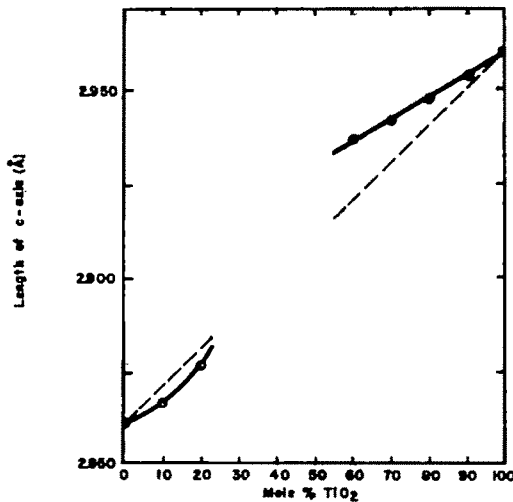


Fig. 6. Length of c-axis for rutile solid solutions.

sample in its platinum holder at 1100°C for 24 hours. No further sintering occurred during the experiment as evidenced by the constancy of room-temperature parameter measurements, before and after the high-temperature run to 1075°C . Slight discontinuities seem to occur at about 1000°C in the expansion curves. In SiO_2 (quartz), the thermal expansion coefficient starts to increase considerably a few degrees below the inversion. At the inversion temperature, it decreases to practically zero and perhaps even becomes negative at temperatures above the inversion. Attempts by McKinstry (personal communication, 1960) to measure a sharp volume change at the inversion have not been very successful. Were it not for the heat effect, although small, the alpha- to beta-quartz inversion in SiO_2 might be considered a second-order transition.

On the basis of the results obtained by differential thermal analysis experiments, a metastable alpha- to beta-quartz inversion in GeO_2 is indicated in figure 4. The stable rutile to quartz inversion is placed at 1049°C , and the melting points as determined by Laubengayer and Morton (1932) are as shown. The positive slope of the boundaries between the various fields of stability seem reasonable if one considers the densities of the various phases:

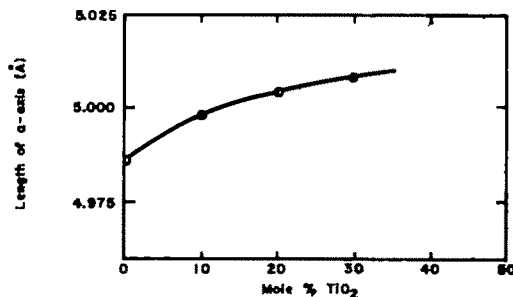


Fig. 7. Length of a-axis for quartz solid solutions.

rutile form, 6.277 g/cc, α -quartz form, 4.280 g/cc, and annealed glass (MacKenzie, 1959), 3.667 g/cc.

The system $\text{GeO}_2\text{-TiO}_2$.—Preliminary heat treatments of compositions in this system indicated that there was only partial solid solubility between the rutile forms of GeO_2 and TiO_2 . Because of large differences in lattice parameters of the end members of the system, the most accurate approach to the determination of phase boundaries was to use measured values of lattice parameters of known composition of solid solutions. The compositions of two solid solutions in equilibrium at any temperature were then obtained by measuring their lattice parameters, using the (200) and (002) reflections for the rutile solid solutions and the (200) reflection for the β -quartz solid solutions.

Figures 5, 6, and 7 show the experimental values of lattice parameter measurements obtained from samples of known composition, which were reacted in small sealed platinum tubes suspended in a quench furnace. The presence of a single homogeneous phase, as shown by X-ray diffraction analysis, was a justification for the assumption that equilibrium was established. The dotted lines in figures 5 and 6 represent the curve on which these parameters would fall if Vegard's Law were applicable. For a composition and temperature where two solid solutions were in equilibrium, it was not necessary to seal the specimens, as small GeO_2 losses would lead only to a change in the relative amounts of the two phases. Using this method, satisfactory results were obtained as shown in table 2 for construction of the equilibrium diagram shown in figure 8. In the case of the rutile-type solid solutions, both a- and c-axis measurements were made and averaged for fixing phase boundaries, the difference in calculated composition never exceeding 2 mole percent. In the quartz-type solid solutions, satisfactory high-angle peaks could not be obtained to measure both parameters.

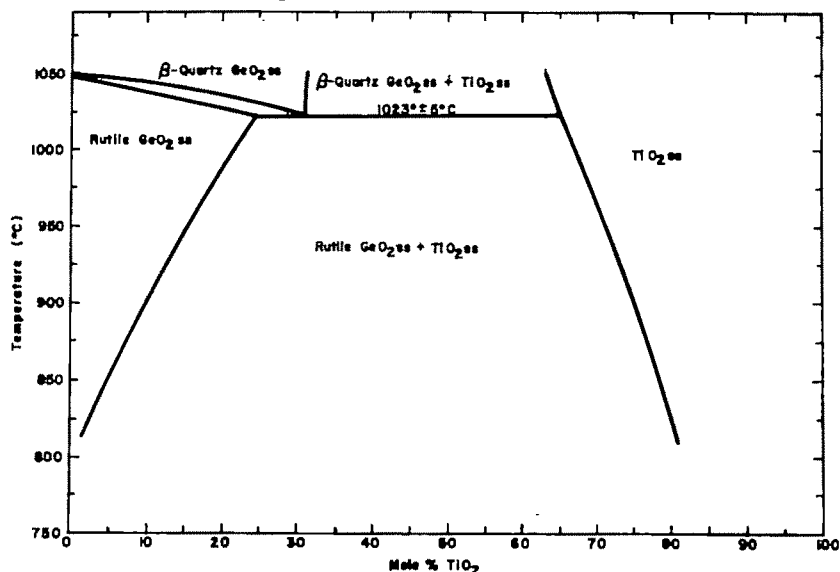


Fig. 8. The system $\text{GeO}_2\text{-TiO}_2$.

TABLE 2

Quench results for the system $\text{GeO}_2\text{-TiO}_2$

Mole % TiO_2	Temp. $^{\circ}\text{C}$	Time (hr)	Phases
10.0	910	13	R- $\text{GeO}_{2.55}$
"	947	22	R- $\text{GeO}_{2.55}$
"	1034	5	R- $\text{GeO}_{2.55}$ (9.5 TiO_2) + Q- $\text{GeO}_{2.55}$
"	1038	6	R- $\text{GeO}_{2.55}$ + Q- $\text{GeO}_{2.55}$ (13.5 TiO_2)
"	1048	6	Q- $\text{GeO}_{2.55}$
20.0	850	15	$\text{TiO}_{2.55}$ + R- $\text{GeO}_{2.55}$ (4.5 TiO_2)
"	890	15	$\text{TiO}_{2.55}$ + R- $\text{GeO}_{2.55}$ (8.0 TiO_2)
"	947	24	$\text{TiO}_{2.55}$ + R- $\text{GeO}_{2.55}$ (15.5 TiO_2)
"	1000	8	R- $\text{GeO}_{2.55}$
"	1025	8	R- $\text{GeO}_{2.55}$
"	1031	2	R- $\text{GeO}_{2.55}$ + Q- $\text{GeO}_{2.55}$ (22 TiO_2)
"	1052	1	Q- $\text{GeO}_{2.55}$
30.0	997	20	$\text{TiO}_{2.55}$ + R- $\text{GeO}_{2.55}$ (21.0 TiO_2)
40.0	1019	12	R- $\text{GeO}_{2.55}$ + $\text{TiO}_{2.55}$
"	1026	16	Q- $\text{GeO}_{2.55}$ + $\text{TiO}_{2.55}$
"	1042	1	Q- $\text{GeO}_{2.55}$ (31.0 TiO_2) + $\text{TiO}_{2.55}$
50.0	1050	24	Q- $\text{GeO}_{2.55}$ + $\text{TiO}_{2.55}$ (63.5 TiO_2)
60.0	855	24	R- $\text{GeO}_{2.55}$ + $\text{TiO}_{2.55}$ (78.0 TiO_2)
"	963	24	R- $\text{GeO}_{2.55}$ + $\text{TiO}_{2.55}$ (69.5 TiO_2)
"	1011	24	R- $\text{GeO}_{2.55}$ + $\text{TiO}_{2.55}$ (66.0 TiO_2)
"	1062	20	$\text{TiO}_{2.55}$
70.0	1003	19	$\text{TiO}_{2.55}$
"	910	19	R- $\text{GeO}_{2.55}$ + $\text{TiO}_{2.55}$ (73.5 TiO_2)
80.0	904	23	$\text{TiO}_{2.55}$
90.0	895	27	$\text{TiO}_{2.55}$

The largest solubility of TiO_2 in the rutile form of GeO_2 occurs at about $1023^{\circ}\text{C} \pm 5^{\circ}$ and corresponds approximately to the composition $\text{Ge}_{0.75}\text{Ti}_{0.25}\text{O}_2$. At 800°C , the solubility is practically zero. According to Roy (personal communication, 1960), the extent of rutile GeO_2 solid solution is decreased with increased pressure.

The greater solubility of TiO_2 in the quartz type may be a manifestation of the more open structure characteristic of compounds having the β -quartz structure. It is noteworthy that in this case the Ti^{4+} ion occurs in tetrahedral coordination.

The maximum solubility of GeO_2 in TiO_2 in the temperature range studied was about 40 mole percent. Sekeras (1959) made firings of bar specimens of the 50 percent GeO_2 , 50 percent TiO_2 composition up to 1300°C without the formation of liquid. Although considerable surface volatilization was evident, it was obvious that the solidus was not below 1300°C . Since GeO_2 melts at about 1116°C , it seems reasonable to assume that the solidus of GeO_2 -quartz solid solutions increases with increasing amounts of TiO_2 in solid solution.

CONCLUSIONS

1. GeO_2 occurs in three forms. The rutile form is stable between room temperature and $1049^\circ\text{C} \pm 5^\circ$. Above this temperature, it changes very slowly to the β -quartz form which melts at $1116^\circ\text{C} \pm 5^\circ$. On cooling, the β -quartz form metastably inverts rapidly and reversibly to the metastable α -quartz form around 1000°C . The metastable α -quartz form is easily retained to room temperature.

2. The maximum solubility of TiO_2 in the rutile and β -quartz forms of GeO_2 is about 25 mole percent and 30 mole percent respectively in the temperature range studied. Solid solution of TiO_2 in GeO_2 lowers the stable rutile to quartz inversion from $1049^\circ\text{C} \pm 5^\circ$ to about $1023^\circ\text{C} \pm 5^\circ$. The solubility of GeO_2 in TiO_2 is about 40 mole percent at temperatures slightly greater than 1050°C .

ACKNOWLEDGMENTS

The author expresses his appreciation to F. A. Hummel and G. W. Brindley for their interest in this investigation, and to the Department of Ceramic Technology of The Pennsylvania State University for financial support. Thanks are also extended to H. A. McKinstry for his helpful suggestions in connection with the high-temperature X-ray diffraction experiments.

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REVIEWS

The Geological Evolution of North America, A Regional Approach to Historical Geology; by THOMAS H. CLARK and COLIN W. STEARN. P. vi, 434; 285 figs. New York, 1960 (Ronald Press Co., \$7.50). *Essentials of Earth History, An Introduction to Historical Geology*; by WILLIAM LEE STOKES. P. x, 502; 376 figs. Englewood Cliffs, New Jersey, 1960 (Prentice-Hall, Inc., \$8.75). —Teachers of elementary geology are showing more and more dissatisfaction with the traditional descriptive-chronologic presentation of Earth history. Many feel that the chronologic organization is wastefully repetitious, and others object to spending most of the second semester on historical description when there is strong and ever-increasing pressure to cover more principles, both geological and physical-chemical, during the first semester.

These criticisms suggest two solutions. One group of historical geology teachers would be satisfied with trying to make the present descriptive content more palatable through reorganization. The other group would devote much more time to stratigraphic and paleontologic principles with a corresponding deletion of descriptive detail, regardless of how appetizingly it might be presented.

Clark and Stearn's book is a refreshingly original product of the reorganization school. The authors have completely abandoned the usual chronologic treatment and have substituted a regional outline of North American history similar to that used in the popular structural syntheses of Philip B. King. The text is divided into five major units: Introduction, The Appalachian Geosyncline, The Cordilleran Geosyncline, The Continental Nucleus and Northland, and The Evolution of Life.

The introduction contains the usual summary treatment of stratigraphic principles and pregeologic history as well as two unique chapters, "The Geosynclinal Theory" and "Epeiric Seas of the Stable Interior".

The bulk of the text is devoted to three major units on the Appalachian Geosyncline, Cordilleran Geosyncline, and Canadian Shield. The history of each of these provinces is treated in a roughly chronologic order with strong emphasis on stratigraphic and tectonic description. Pleistocene history is given a unified treatment in a single chapter. The textual discussion is supplemented by very clear diagrams and excellent generalized facies maps.

The regional organization makes it impossible to combine the physical and biologic aspects of Earth history and therefore the authors have treated the history of life in a separate and final unit. This unit is a chronologically organized description with little discussion of paleontologic principles. The historical paleontology is supplemented by the usual appendix which gives brief systematically organized descriptions of the major taxa of plants and animals.

The writing is clear and polished, although not exciting, and the book is carefully edited and produced. In short, those who prefer to teach from a lucid and up-to-date regional description of North American geologic history need look no further. This book will not, however, satisfy those who feel that the most fundamental and logical framework for teaching Earth history is the chronologic succession of life and landscapes through time. It will also be dis-

appointing to those who are convinced that the beginning student needs exposure to more principles and fewer facts.

Stokes' book, on the other hand, is the first full-scale attempt to include an extended treatment of principles in a historical geology text. Approximately the first fourth of the book is devoted to stratigraphic principles (time, uniformity, sedimentation and superposition, faunal succession, correlation, and classification), the middle half to a worldwide chronologic treatment of physical and biologic history, and the last fourth to paleontologic principles (origin and nature of life, dispersal, adaptability, extinction, and selected family histories). Principles are even stressed in the large middle unit of chronologic description. To cite but two examples, the Precambrian chapter contains a pertinent review of isostasy and the Pleistocene chapter discusses possible causes of continental glaciations.

The book is written in a lively and straight-forward style and is filled with new and effective explanations of the data of Earth history. The photographs and charts are extremely well chosen and include a series of excellent paleogeographic maps of the world for each geologic period.

This is an unusually ambitious book in attempting to cover both principles and worldwide geologic history. In my opinion, it is not only uniquely successful, but is also one of the most original and vital new geology texts to appear in recent years. I predict that it will be among the most popular.

A. L. MC ALESTER

The Geology of the U. S. S. R.; a short outline, including a 1:7,500,000 scale geological map of the U. S. S. R. in full colour; by D. V. NALIVKIN, translated by S. I. TOMKEIEFF. P. 170, 1 fig. and map in 2 sheets. London, New York, 1960 (Pergamon Press, \$15.00).—It is amazing to read in the preface of this book that it is the first comprehensive account of the geology of Russia published in English since 1845, and that its Russian original (published in 1957) was the first for the whole Soviet Union even in Russian. We must therefore be grateful to Dr. Tomkeieff and the Pergamon Press for making it available to us in our own language. No translation can ever be entirely adequate to its original, for those who can read that original, but for those who cannot it opens the door to what would otherwise be inaccessible.

Academician Nalivkin was the chief editor for the three magnificent general maps of the Soviet Union on three different scales that have recently become available; moreover, he has worked actively in many parts of the Soviet Union. Thus his knowledge of the regional geology of his country is unsurpassed, and this account is as complete as one could hope for in a book that describes 15 percent of the Earth's surface in 150 pages. By arrangement with the Soviet geologists, the map on a scale of 7½ million was reprinted in Moscow with an English explanation especially for this translation, adding greatly to its usefulness. For those who need more detail, the great three-volume work on the Geological Constitution of the U. S. S. R. (3 volumes, 1300 pages of Russian, published in 1958), is now appearing in French translation, published by the Centre National de la Recherche Scientifique in Paris.

JOHN RODGERS

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THE COOLING OF IRREGULARLY SHAPED IGNEOUS BODIES

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ABSTRACT. Numerical values are calculated for the temperature in a cooling extrusive sheet, on the assumption that the thermal properties of liquid and solid magma and country rock are the same. The progress of specified isotherms are illustrated for bodies of the following simple geometric shapes: a flow terminated at a vertical plane, a flow and an intrusive sheet with an abrupt change in thickness, a flow with nonuniform initial temperature, a flow and an intrusive sheet with a feeder. Judging from these data, the common assumption that joint columns in cooled igneous bodies are perpendicular to the isotherms is not always valid, especially in regions of sharp curvature of the isotherms and in the last regions to solidify.

Temperatures at the contact between magma and country rock are greatest at internal corners of the magma, and an increase in metamorphism may be expected as such a corner is approached. The effect of latent heat is to raise the temperature at the contact, to slow up the early stages of cooling, and to increase the asymmetry of the temperature distributions, but the pattern of the isotherms is not greatly altered. For calculations such as these, radiation at the upper surface of a flow and pre-heating of the country rock can apparently be neglected.

INTRODUCTION

Calculations of the temperatures in cooling intrusive and extrusive sheets have been in the literature for many years. Formulae for the extrusive sheet were given by Ingersoll and Zobel (1913) and were fully discussed by Lovering (1935), who also considered intrusions in the form of rectangular cylinders, rectangular parallelepipeds, and spheres, as approximations to stocks and laccoliths. In this early work it was assumed that the country rock was initially at a constant temperature which could be taken to be zero, and that the magma was initially at a uniform temperature T_0 . A number of other simplifying assumptions were also made; namely: (i) the effect of the emission of latent heat was neglected, (ii) liquid and solid magma and country rock were all assumed to have the same thermal properties, (iii) the effect of the pre-heating of the country rock that would occur if magma flowed over it for some considerable time before quiescence was neglected, (iv) for extrusives the upper surface was assumed to be at zero temperature. These assumptions are in fact reasonably well justified for the purpose of obtaining a rough quantitative estimate of temperatures in a cooling igneous mass. If they are not made, alterations in detail occur; in fact, calculations allowing for all these effects can be made without difficulty, though at the price of additional complexity. This matter is discussed in the last section.

A rather different approach to the problem of the cooling sheet was made by Lane (1898), who used an approximate method that is, in effect, more complicated and less satisfactory than those referred to above, and his results

are used by Tomkeieff (1940) in a discussion of columnar jointing. The discussion of jointing requires consideration of the cooling of masses of rock of relatively complicated forms. Following Iddings (1886, 1909) and James (1920) geologists have generally assumed that joint columns run normal to the isotherms in the cooling mass, and attempts have been made to estimate the shape of the isotherms, and hence of the intrusion, from directions of jointing. Tomkeieff has injected the additional suggestion that the rate of movement of the isotherms as well as their shape has an important effect on jointing.

Clearly, even for the development of qualitative ideas on jointing such as those mentioned above, some knowledge of the actual shape of the isotherms is needed, and, of course, calculation of temperatures is a necessary preliminary for calculation of thermal stress. The object of this paper is primarily to give accurate drawings of the isotherms in some simple special cases on the simple assumptions stated above. The effects of latent heat, pre-heating of the country rock and so on will usually be to raise temperatures (in a manner discussed in the last section) but they will not greatly affect the *pattern* of the isotherms. Simple rectangular shapes have been chosen since they lead to simple mathematical formulae. It may be expected, however, that if their corners were rounded off slightly (for example, to the shape of the curves $\tau = 0.01$ in the figures) the general pattern would not be changed significantly.

There is one further assumption which must be stated precisely; this is that cooling of the magma takes place by conduction and not by the development of systematic convection cells. One presumes that in thin sheets convection cells do not develop, but in large bodies such as the Skaergaard intrusion they certainly do; in sheets whose thicknesses are several hundred meters they might be expected, but field evidence for their existence is lacking. This paper explores the thermal consequences of the assumption that cooling is by conduction; the thermal consequences of the existence of convection cells would be different and must be studied independently. By comparing consequences of the two possible assumptions it may be possible to make deductions about the actual mechanism of cooling.

ISOTHERMS FOR TWO-DIMENSIONAL REGIONS

In all cases it is assumed, as stated in the Introduction, that the country rock is at zero temperature and that the magma is suddenly emplaced at a uniform temperature T_0 . The temperature T at any point in the magma at time t after emplacement can be calculated from formulae given later, and the isotherms at any time can then be drawn.

As remarked by Lovering (1935), sheets of all thicknesses may be described by the same set of curves if, instead of the actual time t , a quantity τ proportional to it is used which is defined by

$$\tau = \kappa t / d^2, \quad (1)$$

where t is the time after emplacement, d is the thickness of the sheet (or a specified portion of it) and κ is the thermal diffusivity of the material, which is defined as $\kappa = K/\rho c$, where K is the thermal conductivity, ρ the density, and c the specific heat. The quantity τ defined by (1) is in fact dimensionless,

and the units would normally be c.g.s., calorie and $^{\circ}\text{C}$, in which the value of κ for solid dolerite is about 0.007. If we introduce the more convenient units $D = d/100$ for the thickness of the sheet in meters and $t_y = 3.17 \times 10^{-8}t$ for the time in years after emplacement, and use the value of κ for solid dolerite given above, (1) becomes

$$\tau = 22t_y/D^2. \quad (2)$$

Thus, for example, $\tau = 0.01$ corresponds to a time t_y after extrusion of 0.045 years for a flow 10 meters thick, or 1.1 years for a flow 50 meters thick.

Figures 1 to 8 show the position of a specified isotherm at equally spaced intervals of time for a variety of shapes of the igneous body. The chosen isotherms are $0.8 T_0$ and $0.6 T_0$, which, for an initial temperature of $T_0 = 1200^{\circ}\text{C}$ would be 960°C and 720°C .

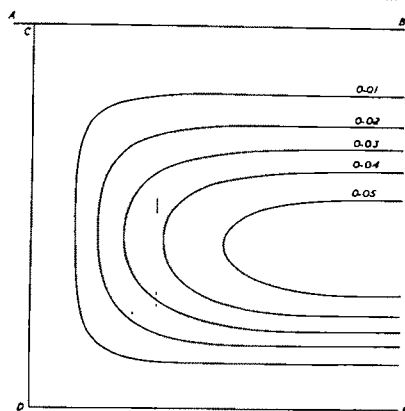


Fig. 1

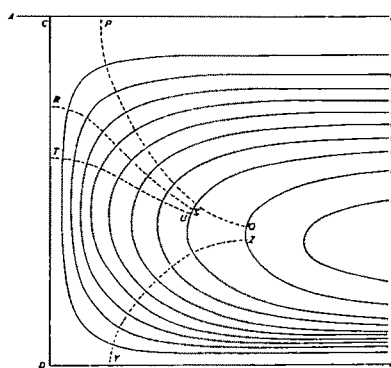


Fig. 2

Fig. 1. Progress of the $0.8 T_0$ isotherm for an extrusive sheet initially at temperature T_0 , occupying the region BCDE of thickness d . The free surface BC is maintained at zero temperature and the region below the surface ACDE contains country rock initially at zero temperature. The numbers on the curves are values of $\tau = \kappa t/d^2$.

Fig. 2. Progress of the $0.6 T_0$ isotherm for the situation of figure 1.

Case (i) A flow terminated at a vertical plane (figs. 1 and 2).—Here the magma occupies the semi-infinite strip BCDE of thickness d , and the country rock is in the region below ACDE. The upper surface ACB of both country rock and magma is at zero temperature. Figure 1 shows the position of the isotherm $0.8 T_0$ at equally spaced intervals of time specified by the values of τ on the curves, and figure 2 shows corresponding curves for the $0.6 T_0$ isotherm. Isotherms for an extrusive that fills a valley with vertical walls may be obtained by combining two figures of this type. As remarked earlier, if the valley, instead of having vertical walls, has a shape similar to the isotherms for $\tau = 0.01$ or 0.02 , the general pattern of the isotherms is not likely to be altered greatly.

Case (ii). A change in the thickness of a flow (figs. 3 and 4).—Here the flow is supposed to have thickness d in the region to the right of DE and thickness $\frac{1}{2}d$ in the region to the left. There is country rock below the boundary CDEF, and the upper surface AB is always at zero temperature. Figures

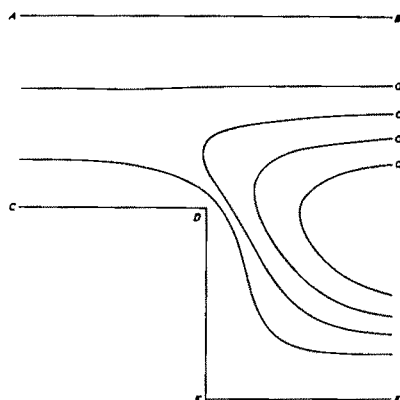


Fig. 3

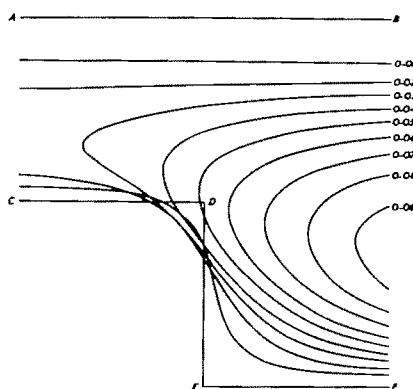


Fig. 4

Fig. 3. Progress of the $0.8 T_0$ isotherm for an extrusive sheet initially at temperature T_0 , whose thickness is d in the region BF and $\frac{1}{2}d$ in the region AC. The free surface AB at zero temperature and the region below CDEF contains country rock initially at zero temperature. The numbers on the curves are values of $\tau = \kappa t / d^2$.

Fig. 4. Progress of the $0.6 T_0$ isotherm for the situation of figure 3.

3 and 4, respectively, show the position of the $0.8 T_0$ and $0.6 T_0$ isotherms for equally spaced values of the time specified by $\tau = \kappa t / d^2$. Their behavior near the point D in figure 4 is noteworthy. For small values of τ , 0.01 and 0.02, the $0.6 T_0$ isotherm moves into the country rock, corresponding to heating of the country rock near D above this temperature, and it subsequently moves away from it in the general process of cooling.

Isotherms for a flow with a localized thickening, as in figure 9, may be obtained by combining two figures of the present type.

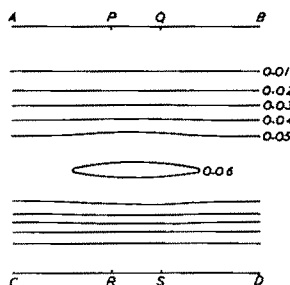


Fig. 5. Progress of the $0.8 T_0$ isotherm in an extrusive sheet of thickness d in which the surface AB is at zero temperature and the region below CD is country rock initially at zero temperature. The magma in the region PQRS is initially at a temperature of $1.05 T_0$, and that in the regions QBDS and APRC at temperature T_0 . The numbers on the curves are values of $\tau = \kappa t / d^2$.

Case (iii) *The effect of non-uniformity of the initial temperature of the magma (fig. 5).*—It is well known that in actual flows the temperature of the magma varies considerably. The effect of such variations may be studied by supposing part of the flow to be at a slightly higher temperature than the remainder. In figure 5 the flow is assumed to have uniform thickness d , to be in

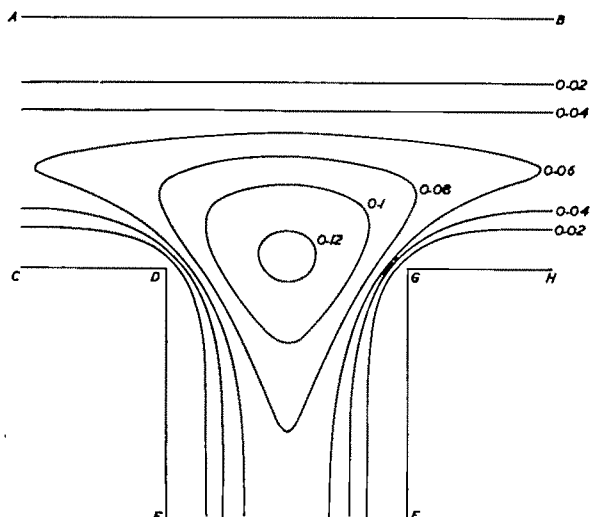


Fig. 6. Progress of the $0.8 T_0$ isotherm in an extrusive sheet ABHC of thickness d with a feeder EDGF of the same thickness. The surface AB is at zero temperature, the magma is initially at temperature T_0 , and the country rock in the regions CDE and HGF is initially at zero temperature. The numbers on the curves are values of $\tau = \kappa t / d^2$.

contact with country rock along CD, and to have its upper surface AB kept at zero temperature. The initial temperature of the flow is assumed to be T_0 except in the rectangular region PQRS, where $PQ = d/5$, in which it is $1.05 T_0$, that is, about 50°C hotter than the rest of the flow. Successive positions of

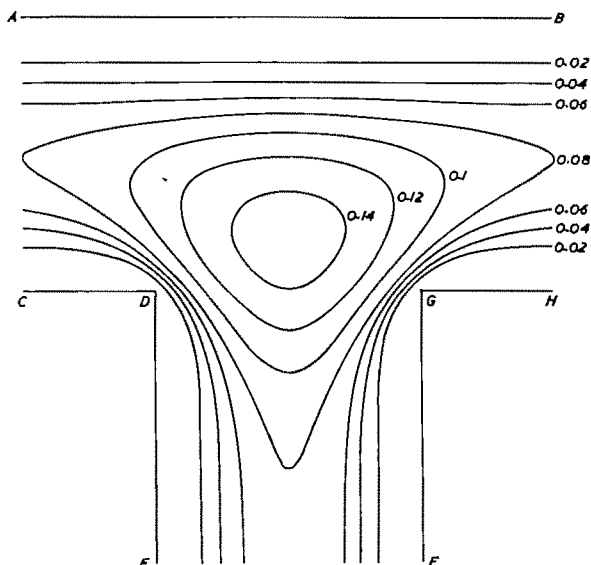


Fig. 7. Progress of the $0.8 T_0$ isotherm in an intrusive sheet ABHC of thickness d with a feeder DGFE of the same thickness. The numbers on the curves are values of $\tau = \kappa t / d^2$.

the $0.8 T_0$ isotherm are shown in figure 5. The effect of the localized hot-spot PQRS is to give a closed isotherm near the center of the flow. If instead of the hot-spot's extending right across the flow it had been near the center of the flow only, there would still have been a closed isotherm near the center; on the other hand, if the hot-spot had been near the upper or lower surfaces of the flow, there would merely have been a slight distortion of the isotherms.

Case (iv) A flow with a feeder (fig. 6).—Here, for simplicity, the feeder DEFG and the flow ABHC are taken to have the same thickness d . Figure 6 shows successive positions of the $0.8 T_0$ isotherm for this case. The hot-spot at the intersection, and its projection into both the flow and the feeder, are noteworthy.

Case (v). An intrusive sheet with a feeder (fig. 7).—The only change from Case (iv) is that the region above the upper surface AB is assumed to consist of country rock initially at zero temperature. Successive positions of the $0.8 T_0$ isotherm are shown in figure 7; they are seen to be very similar in type to those of figure 6, showing that this very considerable change in conditions at the upper surface has little effect on the pattern of movement of the isotherm.

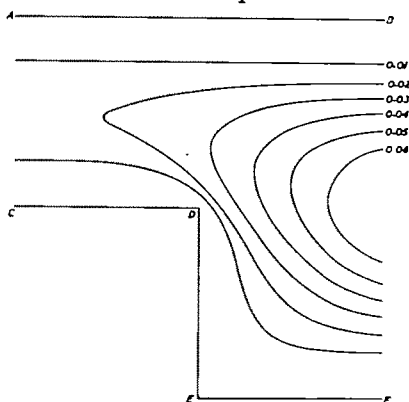


Fig. 8. Progress of the $0.8 T_0$ isotherm in an intrusive sheet, initially at temperature T_0 , whose thickness is d in BF and $\frac{1}{2}d$ in AC. The numbers on the curves are values of $\tau = \kappa t/d^2$.

Case (vi). A change in thickness of an intrusive sheet (fig. 8).—The only change from Case (ii) is that the region above the upper surface AB is assumed to contain country rock. Successive positions of the $0.8 T_0$ isotherm are shown in figure 8.

Figures 1 to 7 illustrate the way in which selected isotherms move in idealized situations of moderate complexity. They are perhaps deceptively simple, since attempts to guess the behavior of the isotherms frequently lead to results very different from the calculated ones. In all cases, the isotherms and their movement are determined by the equation of conduction of heat, which excludes certain types of behavior. When hypothetical isotherms are drawn (for example, to predict directions of jointing), these sets of isotherms, and their movement, must be possible ones for the whole region under consideration. For example, Waters (1960), wishing to explain certain inclined joint columns as being caused solely by inclined isotherms, shows portions of

hypothetical isotherms (his fig. 1), but the writer cannot envisage a complete set of isotherms covering the region in question that will have the required shape, which must be done before Waters' explanation can be regarded as justified.

COLUMNAR JOINTING

It is not the object of this paper to discuss the mechanism of columnar jointing, but certain observations follow from the movement of the isotherms as shown in figures 1-7. As remarked earlier, if it is assumed that columnar jointing is the result of cracking caused by tensile thermal stresses due to contraction, these stresses are controlled by temperature and hence specified by the isotherms. There is no theoretical reason why the maximum tensile stress should be parallel to the isotherms,¹ though this is a reasonable working hypothesis when their curvature is not too great. Drawing curves normal to a series of positions of a moving isotherm, as in the dotted curves of figure 2, becomes relatively difficult as the isotherms contract onto a local hot-spot. Thus, when such a point is approached, the joints may tend to depart from the directions normal to the isotherms. The patterns shown in figure 2 may be looked at in two ways: on a relatively small scale the set PQ, RS, TU, are reminiscent of the common "fan" structure, whereas on a larger scale the sets PQ, YZ suggest the "basin" structure in which horizontally lying joints occur, (cf. Iddings, 1886). This point is referred to below in connection with figure 9.

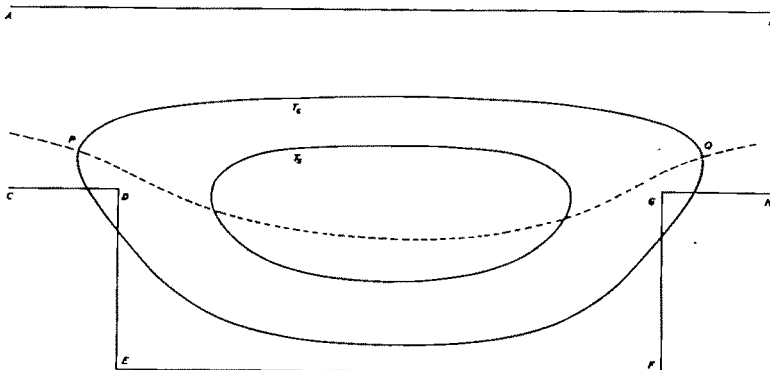


Fig. 9. The relative position of the isotherms $T_1 = 0.8 T_0$ and $T_2 = 0.6 T_0$ at a time given by $kt/d^2 = 0.04$ for a flow filling a valley. The flow is initially at temperature T_0 and its maximum thickness is d .

It is extraordinarily difficult to describe the stress-situation likely to exist in a cooling igneous mass. Judging by observations on modern flows, cracks are formed at a relatively high temperature (above red heat), and for simplicity it might be assumed that there is some temperature T_0 at which cracking occurs, so that cracks might be expected to extend from the surface to the T_0 isotherm. There will also be an isotherm T_c at which solidification is complete.

¹ In certain cases, such as the cooling of spheres or circular cylinders by radial flow of heat, the principal axes of stress are, by symmetry, in and perpendicular to the isotherms provided there are no mechanical constraints applied. In general, however, there are such constraints; for example, if two generators of a circular cylinder are held in fixed positions, the stress-situation in the cylinder would be entirely different from that in the unconstrained cylinder, although the temperature distributions would be identical.

Taking $T_0 = 0.6 T_c$, $T_s = 0.8 T_c$, these isotherms for a flow shaped as in figure 9 are shown in figure 9 for $\tau = 0.04$ (as actual values of T_0 and T_s in the present context, the figures $0.6 T_c$ and $0.8 T_c$ are too low; they were chosen to give diagrams at reasonably widely spaced intervals of temperature).

The process of jointing may then be envisaged as follows: Cracks will start at both the upper surface and the lower contact and at any time will have moved in to near the T_0 isotherm; as long as some magma remains liquid, the two systems of cracks will remain virtually independent, the stresses at the tip of each crack being determined by the thermal situation and by the other cracks proceeding from the same margin. When the whole of the magma has solidified, the stress-situation will be entirely different, since the stresses at the tip of any crack will now be determined by the whole region with all its cracks rather than its upper or lower part. This provides a simple explanation of the commonly observed division of a flow into three parts (Tomkeieff, 1940); the upper and lower sets of columns may have formed while the interior was still liquid, and the center region after solidification was complete. The more complicated stress-situation in this latter case could account for the greater complexity of the jointing in this region, as frequently observed. An additional reason for this complexity is that any irregularity of the surface (fig. 9) or of the initial temperature (fig. 5) may result in a system of closed isotherms near the center of the sheet, and it is reasonable to suppose that a complicated system of isotherms will lead to a complicated stress pattern. In the cases of very uniform flows and intrusions, where the boundaries of the region are relatively flat and the initial temperatures uniform, these complexities might well be absent.

If jointing takes place, as suggested above, by propagation inwards of a number of cracks, it is highly probable that in situations involving curved isotherms some particular crack or cracks will be favored and will propagate more rapidly than others; it is reasonable to suggest that the direction PQ, figure 9, along which the isotherms and hence also the surface of solidification move most rapidly, might be so favored. If this were the case, the whole stress-situation would be altered, and other joints that are propagated more slowly, either from above or below, might be expected to be terminated abruptly at PQ. In this way the well-known "basin" structure (Iddings, 1886; McDougall, 1959), in which some joints run almost horizontally and others intersect them, might be explained.

The general mechanism described above is very similar to that envisaged by James (1920), but the present drawings of calculated instead of hypothetical isotherms make it possible to be more precise. It should be stated that an entirely different explanation for the tripartite division of a flow has been given by Tomkeieff (1940). The rate of movement of the isotherms is greatest at the center and boundaries of a flow, and least at two intermediate points (this effect is shown very clearly in all the figures), and Tomkeieff associated the three major divisions of the flow with the three regions in which the isotherms move rapidly. It seems likely that the rate of movement of the isotherms will have some effect on the process of jointing, though possibly not the major one envisaged by Tomkeieff.

As shown in the last section, the present assumption that joints proceed simultaneously from both the upper and lower surfaces towards the hotter region in the center of the flow implies that jointing takes place at a relatively high temperature—above the contact temperature, which, allowing for latent heat, is probably between 600° and 700°C . It implies also that, since at any time in the early stages of cooling the greatest temperature is slightly nearer to the lower contact than to the upper surface, the length of the set of columns terminating at the lower contact should be of the same order as, but if anything rather less than, the length of the upper set of columns, which terminate in the upper surface. Broadly speaking, this seems to be the case (Tomkeieff, 1940; Waters, 1960), but one interesting exception has been noted by Mathews (1951), who reports a sequence of flows with thicknesses of the order of 200 ft in which the length of the lower set of columns is only about 20 ft. On the present hypothesis this could occur if the time-interval between flows was short, so that the heat lost by a partially cooled flow would chill only a small portion of a subsequent flow and the two would then cool together. This case is discussed in the last section, where the time between flows under the conditions mentioned above is shown to be of the order of eight years.

CONTACT TEMPERATURES

On the simple thermal assumptions made here, the maximum contact temperature for a sheet is one-half the magma temperature. If latent heat is taken into account it will be substantially increased, and it may also be increased by pre-heating of the country rock and also if the conductivity of the country rock is less than that of the magma.

If the margin is not plane there may be further increases. On the simple thermal assumptions of this paper, one simple result is that, at a corner where the magma chamber has an internal angle α , the contact temperature rises on emplacement to a value of $\alpha/2\pi$ times the magma temperature. If $\alpha = \pi$ this gives the value $\frac{1}{2}$ mentioned above. If $\alpha = \pi/2$ as at E, figures 3 and 4, the contact temperature is one-quarter of the magma temperature; if $\alpha = 3\pi/2$, as at D, three-quarters, and so on. Figure 4 shows that in corners of the latter type, where the country rock projects into the magma, the country rock is raised to a higher temperature and kept there longer than near a plane surface. Thus such corners should provide the regions in which the country rock should be most metamorphosed. This may explain why, for example, although the contacts of the Tasmanian dolerites are in general very little metamorphosed, regions do occur in which the sediments have been mobilized; such regions might occur as an internal corner of the intrusion is approached.

THE PROGRESS OF THE SURFACE OF SOLIDIFICATION

Figures 1 to 8 may be used to give an indication of the way in which the surface at which solidification is complete moves in an igneous mass cooling by conduction alone. As shown in the next section, the effect of the emission of latent heat is to raise the contact temperature and to slow up the early stages of the process of cooling, but it will not greatly affect the general pattern of the isotherms.

During the process of cooling, differentiation takes place, and its effect is to concentrate the more acid material into the last regions to solidify. The most common assumption about the mechanism of differentiation is that it proceeds by a process of crystal settling.

To see the effect of this in two dimensions, consider a region shaped as in figure 9. Suppose that the range of solidification is from T_0 to T_s ; then at any time the region outside the T_0 isotherm in figure 9 will be solid, while early-formed crystals in the region between the T_0 and T_s isotherms will settle through the liquid onto the solidified floor. By this process the region within the T_0 isotherm becomes progressively richer in the more acid constituents. This region will finally contract into a small puddle near the geometrical center of the body. Thus, for an intrusion shaped as in figure 9, the most acid material would be concentrated in an area such as the isotherm for $\tau = 0.06$ in figure 8. This puddle of residual liquid would be displaced upwards from its position in figure 8 by the crystals that have fallen to the floor of the intrusion, but the general configuration should not be greatly changed.

NUMERICAL RESULTS

The fundamental numerical information about the cooling of a flow is given in figure 10, which shows the variation of temperature across a flow of

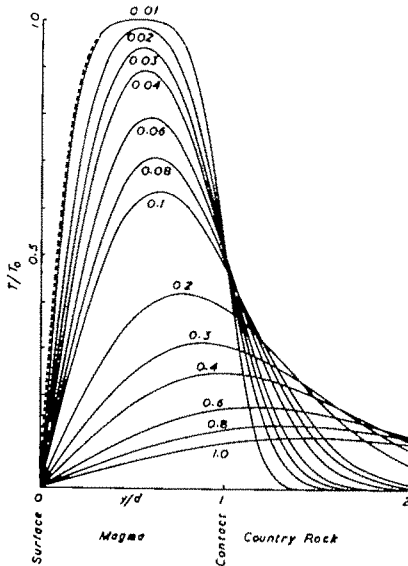


Fig. 10

Fig. 10. The temperature distribution at various times in an extrusive sheet of thickness d with its surface maintained at zero, y is the depth below the surface and the numbers on the curves are values of $\tau = \kappa t/d^2$. The dotted curve is for $\tau = 0.01$ with radiation at the surface.

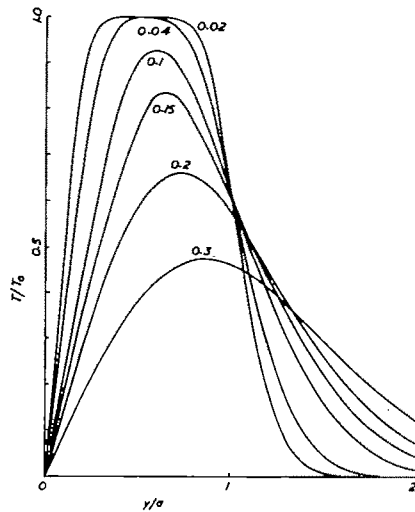


Fig. 11

Fig. 11. The temperature distribution at various times in an extrusive sheet of magma allowing for emission of latent heat of 100 cal/gm over a range of solidification of 1000° to 800°C . The initial temperature of the magma is 1000°C ; the thickness of the sheet is d and y is the depth below its surface; the numbers on the curves are values of $\tau = \kappa t/d^2$ with $\kappa = 0.0071$.

thickness d at various times specified by the quantity $\tau = \kappa t/d^2$ defined in (1) and (2). y is the distance below the surface of the flow.

Many important results follow from inspection of figure 10. For example, the uppermost curve shows that if $\tau < 0.01$, or, by (2), $t_y < 0.00045D^2$, virtually no cooling will have taken place at the center of a flow. For a flow of thickness $D = 10$ meters this time is 0.045 years, and for 50 meters it is 1.1 years.

From the lowest curve, $\tau = 1$, in figure 10, it follows that the whole of the flow has cooled to temperatures of less than $T_0/10$ or about 100°C after a time of $0.045D^2$, that is, 4 years for a 10-meter flow or 100 years for a 50-meter flow. After such times a second flow would be quite unaffected by the heat remaining in an earlier one.

One important point mentioned above in connection with columnar jointing remains to be discussed. The graphs of figure 10 show that for $\tau < 0.4$ the temperature has a maximum within the flow, and that if $\tau < 0.1$ this maximum is quite pronounced. This is consistent with the process envisaged earlier by which jointing begins independently at the upper and lower surfaces and propagates towards the hotter region inwards. Clearly, if this is the case, jointing must occur at a higher temperature than the contact temperature. Also, since the maxima of the curves of figure 10 are always nearer to the lower contact than to the upper surface of the flow, the lengths of the columns beginning at the lower contact (colonnade) would be less than though not very different from those extending from the upper surface. On the other hand, there is no a priori reason why jointing should not take place at lower temperatures, say less than $\frac{1}{2}T_0$. Figure 10 shows, however, that the contact does not fall below this temperature until fairly late in the cooling history of the flow, say $\tau > 0.1$, at which time solidification would long have been complete. At such times the temperature distribution is highly asymmetrical and a totally different pattern of thermal stress would result which would not be likely to lead to a tripartite division of the flow.

The formulae from which the temperature distributions of figure 10 have been calculated are derived in Ingersoll and Zobel (1913) ¶86(53) or Carslaw and Jaeger (1959) ¶2.4(14). Mathematically they may be stated as follows:

Suppose that the magma is initially at a uniform temperature T_0 and the country rock at zero temperature. Suppose also that for all times $t > 0$ after extrusion the upper surface of the magma is maintained at zero temperature. Then if the magma occupies the region $0 > y > -d$ and country rock the region $y < -d$ the temperature T at depth y at time t is given by

$$T/T_0 = \frac{1}{2} \left\{ \operatorname{erf} \frac{y+d}{2d\tau^{1/2}} + \operatorname{erf} \frac{y-d}{2d\tau^{1/2}} - 2 \operatorname{erf} \frac{y}{2d\tau^{1/2}} \right\}, \quad (3)$$

where $\operatorname{erf} x$ is the tabulated error function defined by

$$(4) \quad \operatorname{erf} x = \frac{2}{\pi^{1/2}} \int_0^x e^{-u^2} du,$$

and τ is the dimensionless parameter defined in (1) or (2).

The extension to the two-dimensional regions discussed earlier leads also to simple formulae involving error functions. For example in Case (i) above,

the magma occupies the semi-infinite strip BCDE, $0 > y > -d$, $x > 0$ and the temperature T at (x, y) at time t is given by

$$\frac{T}{T_0} = \frac{1}{4} \left\{ 1 + \operatorname{erf} \frac{x}{2d\tau^{1/2}} \right\} \left\{ \operatorname{erf} \frac{(y+d)}{2d\tau^{1/2}} + \operatorname{erf} \frac{(y-d)}{2d\tau^{1/2}} - 2 \operatorname{erf} \frac{y}{2d\tau^{1/2}} \right\}. \quad (5)$$

The effect on the temperature distributions of figure 10 caused by relaxing the assumptions made earlier may now be considered. Firstly, the free surface was assumed to be at zero temperature while, in fact, it cools by radiation. It is well known, however, that the surface cools very rapidly, and it is frequently reported that flows can be walked on after one or two days; assuming, for example, that the surface temperature has fallen to $0.05 T_0$ after two days, a numerical estimate of the rate of radiation and calculations for a flow of thickness 4 meters (Carslaw and Jaeger, 1959, §14.2) gives the dashed curve for $\tau = 0.01$ in figure 10. This differs so little from the corresponding curve for zero surface temperature that the assumption that the free surface is always at zero temperature is perfectly adequate for the present purposes.

The effect of latent heat of solidification may be taken into account as in Jaeger (1957, 1959). Calculations of the same type have been made for an extrusive sheet of thickness d with its upper surface at zero temperature, its thermal diffusivity $\kappa = 0.0071$ that of dolerite, and latent heat of 100 cal/gm liberated over a range of solidification of 1000° to 800°C . These values, which are rather low, are used because they enable comparison to be made with the corresponding calculations for an intrusive sheet given by Jaeger (1957). The initial temperature T_0 of the magma is taken to be 1000°C . The temperature distribution for various values of $\tau = \kappa t/d^2$ is shown in figure 11. As always,

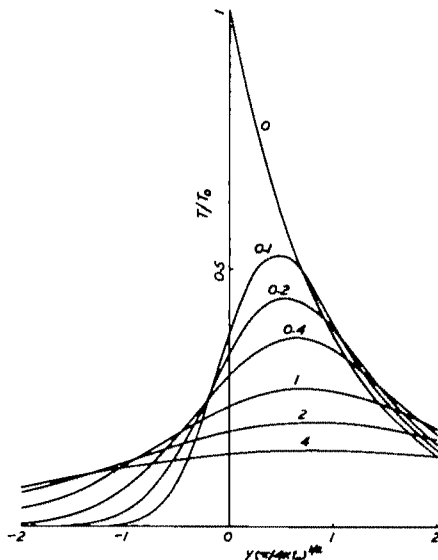


Fig. 12. Temperature distribution at time t in the infinite solid $-\infty < y < \infty$ if the initial temperature is zero in the region $y < 0$, and if the region $y > 0$ is pre-heated by maintaining $y = 0$ at temperature T_0 for time t_0 . The numbers on the curves are the values of t/t_0 .

the effect of latent heat is to raise the contact temperature, which in this case becomes $0.62 T_0$ in place of $0.5 T_0$ in figure 10, and to slow up the early stages of cooling. The asymmetry of the temperature distributions, mentioned earlier, is also increased. Comparison of figures 10 and 11 suggests that in two-dimensional cases the pattern of the isotherms will not be greatly altered.

The effects of dissimilar thermal properties of the various materials have been studied by Lovering (1936, 1955) and Jaeger (1959).

Finally, the effect of pre-heating of the country rock may be considered. Assume that magma at temperature T_0 flows for time t_0 over the country rock before quiescence and the beginning of cooling and solidification, and that the country rock (the region $y > 0$) was at zero temperature before the flow began. The surface of the country rock ($y = 0$) will be maintained at constant temperature T_0 for a time t_0 after which time the temperature at depth y will be

$$T_0 \left\{ 1 - \operatorname{erf} \frac{y}{2(\kappa t_0)^{1/2}} \right\}, \quad (6)$$

which for the present purposes is sufficiently near to $T_0 \exp \{-y(\pi/4\kappa t_0)^{1/2}\}$ for which calculations are easily made. The effect of this additional heat in the early stages of the cooling of the flow is simply to add to the temperatures of figure 10 those calculated for the infinite solid with this initial distribution of temperature; these are shown in figure 12 for various values of the ratio t/t_0 . In this figure the region $y > 0$ corresponds to country rock and $y < 0$ to magma. It appears, for example, that there is a temporary rise above $T_0/10$ within a distance of approximately $3(\kappa t_0/\pi)^{1/2}$ from the contact; for t_0 equal to 2 days this distance is 60 cm. Thus in many cases at least, such effects will be superficial.

The same figure, for cooling instead of heating, may also be used to estimate the effect of a second flow on top of a partially cooled earlier one. If the time interval between the flows is short, the heat lost by the partially cooled flow would chill only a small portion of the second flow, and the two would subsequently cool together. For the example mentioned above (Mathews, 1951), in which there are 6 meters of colonnade in the second flow, let us suppose this involves lowering the temperature by at least $T_0/5$ in this region. It follows from figure 12 that the temperature in the second flow is lowered by an amount greater than $T_0/5$ for a distance y from the contact given by $y(\pi/4\kappa t_0)^{1/2} = 0.4$; taking $y = 6$ meters, $\kappa = 0.0071$, this gives about eight years for the time t_0 between the two flows.

ACKNOWLEDGMENT

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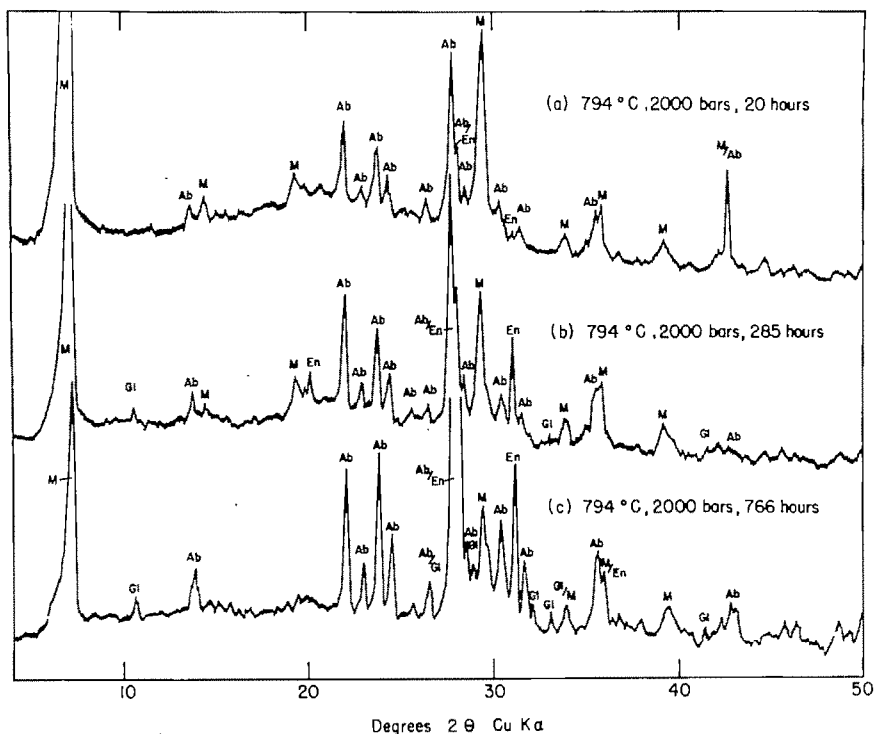


Fig. 1. Growth study of stable and metastable phases obtained for the bulk composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ + excess water within the stability field of glaucophane. Sodic montmorillonite is presumed to be metastable because glaucophane and the high-temperature assemblage of equivalent bulk composition grow at its expense. Positions of X-ray diffraction peaks for sodic montmorillonite indicate partial dehydration. Abbreviations used throughout this paper are listed in table 1.

the breakdown products (high-temperature assemblage of bulk compositions equivalent to glaucophane and quartz + glaucophane) is indistinguishable from that synthesized from an oxide mixture or from glass. The refractive indices of synthetic glaucophane lie between those of an iron-poor natural specimen from Zermatt, Switzerland (Kumitz, 1930, p. 198), and values of a theoretical end member extrapolated by Winchell and Winchell (1951, p. 441) using natural members of the glaucophane-riebeckite series.

TABLE 1
Abbreviations used in this paper

Ab = albite	Tr = tridymite
Cr = cristobalite	V = vapor
En = enstatite	() = enclose phases interpreted as metastable
Fo = forsterite	? = presence not definitely established
Gl = glaucophane	mix = oxide mixture
L = liquid	condensed starting material prefix:
M = sodic montmorillonite	Gl = $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$
Pr = protoenstatite	Q + Gl = $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$
Q = quartz	
Tc = talc	

TABLE 2

Micrometric analyses of condensed run products within the amphibole field of stability for the bulk compositions $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 + \text{H}_2\text{O}$ and $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 + \text{H}_2\text{O}$

Condensed Starting Material	Temp. in °C	P _{vapor} in bars	Duration in hours	Relative Modal Proportions of Metastable Phases				Total Vol. percent Gl
				Fo	En	Ab	Q	
Gl mix	852	175	500	15	10	75	0	14
Gl mix	841	300	232	16	11	73	0	11
Gl mix	830	305	246	13	12	75	0	7
Gl mix	826	1200	142	16	12	72	0	15
Gl glass	760	2000	221	14	10	76	0	22
Computed proportions for the bulk composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$				15.8	11.4	72.8	0.0	
Q + Gl mix	814	505	280	0	32	62	6	7
Computed proportions for the bulk composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$				0.0	29.6	63.3	7.1	

(1050-1250 points counted for each sample)

TABLE 3

Optical properties of synthetic and natural glaucophane

Condensed Starting Material	Temp. in °C	P _{vapor} in bars	Duration in hours	N _x	N _z	Extinction Angle Z $\wedge$ c in °
Gl mix	862	1875	6	1.594	1.620	9
Gl mix	857	1690	10	1.595	1.620	10
Fo + En + Ab	850	825	185	1.596	1.620	9
Gl mix	850	825	185	1.596	1.620	7
Gl mix	840	825	168	1.596	1.619	8
Gl mix	830	175	500	1.596	1.620	9
Gl glass	815	1000	1920	1.595	1.621	10
Fo + En + Ab	794	2000	776	1.595	1.620	8
Gl mix	794	2000	776	1.594	1.620	10
Gl mix	794	2000	285	1.596	1.619	6
Fo + En + Ab	776	800	280	1.594	1.620	8
Gl mix	652	2500	870	1.594	1.620	11
En + Ab + Q + Gl	852	250	991	1.594	1.620	11
Q + Gl mix	836	1730	38	1.596	1.620	14
Tc + Ab	815	1000	1920	1.595	1.621	10
En + Ab + Q	792	1500	480	1.595	1.620	14
Tc + Ab	789	1510	474	1.594	1.618	6
En + Ab + Q	745	2000	332	1.594	1.621	12
Q + Gl mix	745	2000	332	1.594	1.620	11
Q + Gl mix	702	2020	240	1.594	1.619	8
Winchell and Winchell (1951) projected end member				1.586	1.613	8
Kunitz (1930) iron-poor glaucophane (~85 glaucophane, ~15 riebeckite)				1.606	1.627	8

All measurements of synthetic material performed using white light, index oils of 0.002 interval, and corrected for temperature variation; indices of refraction considered accurate to within ± 0.003 , extinction angles to within $\pm 4^\circ$.

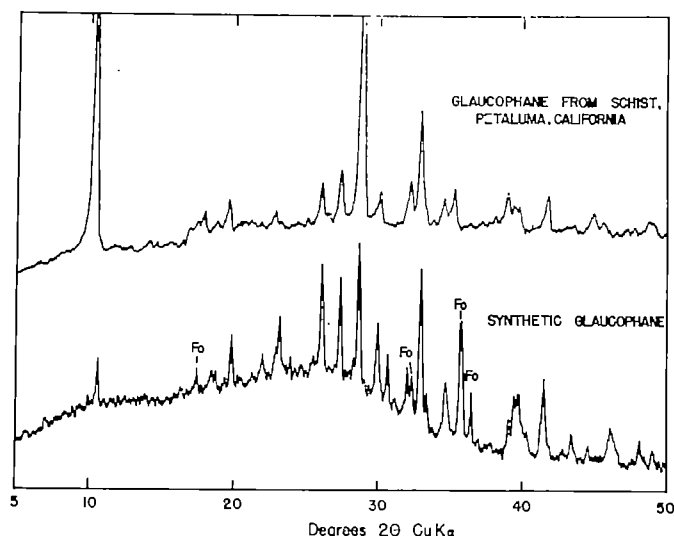


Fig. 2. X-ray diffractometer patterns for synthetic and natural glaucophane; differences in amplitudes of corresponding peaks suggest preferred orientation of the natural specimen. The synthetic material contains the additional phases forsterite and glass.

Glaucophane X-ray Data

In figure 2 the X-ray diffractometer pattern of synthetic glaucophane is compared with that of a natural sample from Petaluma, California, supplied by A. Pabst, University of California. The synthetic material was indexed by comparison with synthetic magnesioriebeckite (Ernst, 1960, table 14). Five peaks were measured (see table 4) using Lake Toxaway quartz as an internal standard. From these measurements, cell dimensions and Q values were calculated. Table 5 presents d values, intensities, Q values, and 2θ values for all measured diffraction peaks of synthetic glaucophane.

In table 6 lattice parameters and cell volumes of synthetic glaucophane and synthetic magnesioriebeckite are compared. The latter has a larger unit cell because the ionic radius of ferric iron exceeds that of aluminum. Some natural glaucophanes have unit cell dimensions smaller than those of the synthetic analogue; deviation of the natural material from the stoichiometric pro-

TABLE 4
Averages of six measurements of X-ray diffraction peaks for
synthetic glaucophane (space group $C2/m$)

Reflection	$2\theta_{av.}^*$	Standard (Chart) Error of the Mean
040	19.814	± 0.0060
131	26.114	± 0.0041
310	28.691	± 0.0054
151	33.000	± 0.0064
202	35.894	± 0.0068

* $CuK\alpha = 1.5418 \text{ \AA}$.

TABLE 5
X-ray powder data for synthetic glaucophane (space group C2/m)

Reflection	$2\theta_{\text{obs}}^*$	Q_{calc}	ΔQ	I	d in Å
020	9.82	.01245	.00013	9	9.00
110	10.56	.01425	.00001	32	8.38
111	18.42	.04306	-.00001	12	4.818
040	19.814	.04981	.00000	36	4.481
111	21.95	.06100	.00000	19	4.049
131	23.19	.06796	-.00003	35	3.885
131	26.114	.08591	.00001	72	3.412
240	27.38	.09434	.00009	65	3.257
310	28.691	.10331	.00000	91	3.120
221	29.99	.11271	.00009	50	2.980
151	30.69	.11777	-.00004	34	2.913
330	32.04	.12821	.00006	24	2.794
151	33.000	.13572	-.00001	100	2.714
331	33.40	.13907	.00013	20	2.683
241	34.76	.15007	-.00010	32	2.581
202	35.894	.15977	.00000	81	2.502
351	39.14	.18888	.00005	18	2.301
331	} 39.79	{ .19292 }	—	25	2.265
080					
261	41.56	.21233	.00059	50	2.173
202	43.49	.23156	.00061	15	2.081
351	44.63	.24272	.00017	9	2.031
242	48.23	.26137	.00044	16	1.887

* $\text{CuK}\alpha = 1.5418 \text{ Å}$

$\Delta Q = Q_{\text{calc}} - Q_{\text{obs}}$

Intensities estimated from peak height.

portions $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 \cdot \text{H}_2\text{O}$, or the existence of two glaucophane polymorphs (Ernst, 1959) may account for this discrepancy.

EXPERIMENTAL RESULTS

Run Data

Tables 7 and 8 present the results of hydrothermal investigation of the bulk compositions $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ + excess water and $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$ + excess water. Three experiments employing the bulk composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ + excess water (quartz + glaucophane + vapor = enstatite + albite + vapor) are listed at the end of table 8.

TABLE 6

Unit cell dimensions of synthetic glaucophane and magnesioriebeckite
(space group C2/m)

Synthetic Glaucophane	Synthetic Magnesioriebeckite
a = 9.71 Å	a = 9.79 Å
b = 17.92 Å	b = 18.02 Å
c = 5.27 Å	c = 5.28 Å
$\beta = 102.6^\circ$	$\beta = 102.6^\circ$
cell volume = 895.4 Å ³	cell volume = 908.6 Å ³

TABLE 7

Results of investigations of the composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$
with excess water

Condensed Starting Material	Temp. in °C	P _{vapor} in bars	Duration in hours	Condensed Run Products
Curve: Fo + En + Ab + Gl + V				
mix	840	175	500	Gl (+ Fo + En + Ab)
mix	852	175	500	Fo + En + Ab + Gl
Fo + En + Ab	852	180	500	Fo + En + Ab + Gl?
mix	841	300	232	Gl (+ Fo + En + Ab)
Fo + Gl + L	856	302	402	Fo + En + Ab + Gl
mix	856	302	402	Fo + En + Ab + Gl
glass	865	300	279	Fo + En + Ab
mix	863	390	194	Fo + En + Ab
mix	847	500	283	Gl (+ Fo + En + Ab)
mix	861	500	259	Fo + En + Ab + Gl
mix	873	500	162	Fo + En + Ab
Fo + En + Ab	860	820	184	Gl (+ Fo + En + Ab)
mix	860	820	184	Gl (+ Fo + En + Ab)
Fo + En + Ab + Gl	866	815	163	Fo + En + Ab
mix	853	1000	139	Gl (+ Fo + En + L)
mix	865	1020	117	Fo + En + Ab
mix	859	1310	66	Gl (+ Fo + En + Ab)
Fo + En + Ab + Gl	862	1210	96	Fo + En + Ab + Gl?
Fo + En + Ab	862	1210	96	Fo + En + Ab
glass	871	1240	118	Fo + En + Ab (+ L)
mix	857	1520	100	Gl (+ Fo + En + Ab)
mix	867	1490	99	Fo + En + Ab + L
Fo + En + Ab	868	1500	79	Fo + En + L
Field: Gl + V				
mix	830	175	500	Gl (+ Fo + En + Ab)
mix	820	240	2215	Gl (+ Fo + En + Ab)
mix	830	305	246	Gl (+ Fo + En + Ab)
Fo + En + Ab	835	295	473	Gl (+ Fo + En + Ab)
Fo + En + Ab	776	800	280	Gl (+ Fo + En + Ab)
mix	785	800	717	Gl (+ Fo + En? + Ab)
Fo + En + Ab	803	820	187	Gl (+ Fo + En + Ab)
mix	803	820	187	Gl (+ Fo + En? + Ab)
Fo + En + Ab + Gl	833	800	159	Gl (+ Fo + En + Ab)
mix	840	825	168	Gl (+ Fo + En + Ab)
Fo + En + Ab	850	825	185	Gl (+ Fo + En + Ab)
mix	850	825	185	Gl (+ Fo + En + Ab)
glass	815	1000	1920	Gl (+ Ab + M)
mix	822	1000	208	Gl (+ Fo + En? + Ab + M)
mix	835	1005	93	Gl (+ Fo + En + Ab)
Fo + En + Ab + Gl	835	950	313	Gl (+ Fo + En + Ab)
Fo + En + Ab + Gl	840	950	315	Gl (+ Fo + En + Ab)
mix	843	1030	142	Gl (+ Fo + En + Ab)
mix	846	1000	89	Gl (+ Fo + En + Ab)
mix	821	1210	64	Gl (+ Fo + En + Ab)
mix	826	1200	142	Gl (+ Fo + En + Ab)
mix	846	1200	142	Gl (+ Fo + En + Ab)
mix	846	1300	25	Gl (+ Fo + En? + Ab)
Fo + En + Ab	859	1310	66	Gl (+ Fo + En + Ab)
mix	797	1500	355	Gl (+ Fo? + En + Ab + M)
mix	843	1490	142	Gl (+ Fo + L)
mix	857	1690	10	Gl (+ Fo + En + Ab? + L)
glass	760	2000	221	Gl (+ Fo + En + Ab)

TABLE 7 (Continued)

Condensed Starting Material	Temp. in °C	P _{vapor} in bars	Duration in hours	Condensed Run Products
mix	794	2000	20	(En + Ab + M)
mix	794	2000	285	Gl (+ En + Ab + M)
mix	794	2000	766	Gl (+ En + Ab + M)
Fo + En + Ab	794	2000	766	Gl (+ En + Ab + M)
mix	818	2000	210	Gl (+ Fo + En + Ab)
mix	823	2000	264	Gl (+ Fo + L)
Fo + En + Ab	843	2000	94	(Fo + En + Ab + M)
Fo + En + Ab	857	1980	18	(Fo + En + L + M?)
mix	862	1990	2	Gl (+ Fo + En + L)
mix	602	2500	1102	Gl (+ Ab + M)
mix	652	2500	870	Gl (+ Ab + M)
mix	701	2520	741	Gl (+ Ab + M)
mix	377	4650	1129	(Ab + M)
mix	502	4400	1104	Gl? (+ Ab + M)
Curve: Fo + En + Gl + L + V				
mix	857	1520	100	Gl (+ Fo + En + Ab)
mix	867	1490	99	Fo + En + Ab + L
Fo + En + Ab	868	1500	79	Fo + En + L
mix	863	1690	14	Gl (+ Fo + En + L)
Fo + En + Gl + L	869	1700	5	Fo + En + L
mix	862	1875	6	Gl (+ Fo + En? + M)
Fo + En + L	862	1990	2	Gl (+ Fo + En + L)
Fo + En + Gl + L	866	1980	2	Gl (+ Fo + En + L)
Fo + En + Gl + L	873	1980	2	Fo + En + L
Field: Fo + En + L + V				
mix	879	1960	5	Fo + En? + L
Fo + En + Ab	879	1960	5	Fo + En + L
Curve: Fo + En + Ab + L + V				
glass	986	300	115	Fo + En + Ab
Fo + En + Ab	997	295	162	Fo + Ab + L
glass	997	295	162	Fo + Ab + L
Fo + En + Ab	955	510	92	Fo + En + Ab
glass	955	510	92	Fo + En + Ab (+ L)
Fo + En + Ab	964	510	93	Fo + En + Ab? + L
glass	964	510	93	Fo + En + L
glass	915	800	120	Fo + En + Ab
glass	891	1000	115	Fo + En + Ab
Fo + En + Ab	908	1010	77	Fo + En + L
glass	909	1000	135	Fo + En + L
mix	857	1520	100	Gl (+ Fo + En + Ab)
mix	867	1490	99	Fo + En + Ab + L
Fo + En + Ab	868	1500	79	Fo + En + L
Fo + En + Ab	843	2000	94	(Fo + En + Ab + M)
Fo + En + Ab	857	1980	18	(Fo + En + L + M?)
Field: Fo + En + Ab + V				
mix	803	1	330	Fo + En + Ab
mix	890	1	2215	Fo + En + Ab
mix	929	1	234	Fo + En + Ab
mix	983	1	162	Fo + En + Ab
glass	1074	1	46	Fo + En + Ab (+ L)
mix	882	260	232	Fo + En + Ab
mix	898	270	99	Fo + En + Ab
glass	912	300	161	Fo + En + Ab
glass	940	293	191	Fo + En + Ab

TABLE 7 (Continued)

Condensed Starting Material	Temp. in °C	P _{vapor} in bars	Duration in hours	Condensed Run Products
glass	948	293	191	Fo + En? + Ab
glass	960	300	66	Fo + En + Ab
glass	975	300	135	Fo + En + Ab
glass	925	500	190	Fo + En + Ab
glass	931	450	122	Fo + En + Ab
glass	939	450	122	Fo + En + Ab
glass	902	755	164	Fo + En + Ab
Curve: Fo + Ab + L + V				
Fo + En + Ab	997	295	162	Fo + Ab + L
glass	997	295	162	Fo + Ab + L
Fo + En + Ab	1005	300	120	Fo + L
glass	1005	300	120	Fo + L
Field: Fo + Ab + L + V				
Fo + En + Ab	997	295	162	Fo + Ab + L
glass	997	295	162	Fo + Ab + L
Curve: Fo + En + L + V				
Fo + En + Ab	955	510	92	Fo + En + Ab (+ L)
glass	955	510	92	Fo + En + Ab (+ L)
Fo + En + Ab	964	510	93	Fo + En + Ab? + L
glass	964	510	93	Fo + En + L
Curve: Fo + En + L + V				
Fo + En + Ab	920	1010	77	Fo + En + L
Fo + En + Ab	899	1400	76	Fo + En? + L
Fo + En + Ab	905	1520	4	Fo + L
Fo + En + Ab	888	2000	4	Fo + En + L
Fo + En + Ab	896	1980	4	Fo + L
Field: Fo + L + V				
Fo + En + Ab	1028	300	120	Fo + L
Fo + En + Ab	900	2000	4	Fo + L

Metastable Sodic Montmorillonite

Difficulties arose from the formation of a fine-grained hydrous silicate within the glaucophane field at temperatures as high as approximately 850°C at 2000 bars vapor pressure. As indicated in table 9, this phase has the X-ray properties of a member of the montmorillonite group. The basal spacing of 15.3 Å is reduced to 12.3 Å either by heat treatment or by quenching runs at diminished pressure. Basal spacings of approximately 17 Å have been obtained by treatment with ethylene glycol. Complete decomposition of this phase at 900°C and 1 atm total pressure yields enstatite + minor nepheline; weight loss indicates that the material with a basal spacing of 12.3 Å contains 6 ± 2 weight percent H₂O. From the relative proportions of breakdown products deduced by X-ray and optical examination, the montmorillonite is estimated to have the approximate formula: $\text{Na}_{1/2}\text{Mg}_3\text{Al}_{1/2}\text{Si}_{3-1/2}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$.

Stability relations for minerals of the montmorillonite group presented by Ames and Sand (1958) indicate that soda-bearing trioctahedral varieties are stable at elevated temperatures. At 1000 atm vapor pressure, montmorillonite

TABLE 8

Results of investigation of the composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$
with excess water

Condensed Starting Material	Temp. in °C	P _{vapor} in bars	Dura- tion in hours	Condensed Run Products
Curve: En + Ab + Q + Gl + V				
En + Ab + Q	847	150	403	En + Ab + Q
Tc + Ab	843	245	187	Q (+ En + Ab)
mix	843	245	187	Gl (+ En + Ab + L)
En + Ab + Q + Gl	852	250	991	En + Ab + Q + Gl
Tc + Ab	842	515	134	Q + Gl? (+ En + Ab + M)
mix	842	515	134	Gl (+ En + Ab + L)
Tc + Ab	855	490	234	En + Ab + Q
mix	855	490	234	En + Ab + Q + Gl
Tc + Ab	866	490	234	En + Ab + Q
Field: Q + Gl + V				
mix	827	250	160	Q? + Gl (+ En + Ab + L)
mix	792	505	280	Q? + Gl (+ En + Ab)
Tc + Ab	800	500	241	Q + Gl (+ En + Ab)
Tc + Ab	814	505	280	Q + Gl (+ En + Ab)
mix	814	505	280	Q + Gl (+ En + Ab)
Tc + Ab	807	1010	278	Q + Gl? (+ En + Ab)
Tc + Ab	815	1000	1920	Q + Gl (+ En + Ab + M)
mix	770	1505	170	Q + Gl (+ En + Ab + M)
mix	702	2020	240	Q + Gl (+ En + Ab)
Curve: En + Q + Gl + L + V				
Tc + Ab	817	1000	622	Q + Gl (+ En + Ab)
Tc + Ab	823	1000	311	En + Q + Gl + L (+ Ab)
Tc + Ab	827	1005	356	En + Gl + L (+ Ab)
mix	827	1005	356	En + Gl + L
En + Ab + Q	782	1500	494	En + Q + L (+ Ab + M)
mix	782	1500	494	Gl + L (+ Ab + M)
Tc + Ab	789	1510	474	En + Q + Gl + L (+ Ab + Tc + M)
En + Ab + Q	789	1510	474	En + Q + Gl? + L? (+ Ab)
Tc + Ab	792	1500	480	En + Gl + L (+ Ab + M)
En + Ab + Q	792	1500	480	En + Gl + L (+ Ab + M)
En + Ab + Q	745	2000	332	Q + Gl (+ En + Ab + M)
mix	745	2000	332	Q? + Gl (+ En + Ab + L)
En + Ab + Q	756	1995	440	En + Q + Gl + L (+ Ab + M)
mix	756	1995	440	En + Gl + L (+ Ab)
En + Ab + Q	763	2000	438	En + Gl + L (+ Ab)
mix	763	2000	438	En + Gl + L (+ Ab)
Field: En + Gl + L				
Tc + Ab	839	1000	87	En + L (+ Ab)
mix	839	1000	87	En + Gl + L
mix	841	1175	240	En + Gl + L
Tc + Ab	836	1730	38	En + Gl + L (+ Tc)
mix	836	1730	38	En + Gl + L
En + Ab + Q	770	2000	423	En + Gl + L (+ Ab)
En + Ab + Q	780	1990	264	En + Gl? + L (+ Ab + M)
mix	780	1990	264	En + Gl + L (+ Ab + M)
En + Ab + Q	795	2000	325	En + Gl + L (+ Ab + M)
Tc + Ab	811	2020	239	En + Gl? + L (+ Ab + M)
mix	811	2020	239	En + Gl + L (+ Ab)
Tc + Ab	820	2000	151	En + L (+ Ab + M)

TABLE 8 (Continued)

Condensed Starting Material	Temp. in °C	P _{vapor} in bars	Duration in hours	Condensed Run Products
mix	820	2000	151	En + Gl + L (+ Ab)
Tc + Ab	832	1990	48	En + L (+ M)
mix	832	1990	48	En + Gl + L
mix	843	2000	33	En + Gl + L
mix	851	1990	3	En + Gl + L
Curve: En + Gl + L + V				
Tc + Ab	860	1500	21	En + Gl + L (+ Tc)
mix	860	1500	21	En + Gl + L
En + Tc + Gl + L	868	1520	49	En + L
En + Gl + L	868	1520	49	En + Gl? + L
En + Ab + Gl + L	861	1990	2	En + Gl + L
En + Gl + L	863	2000	6	En + Gl + L
mix	863	2000	6	En + Gl + L
En + Gl + L	868	1995	4	En + L
mix	868	1995	4	En + L (+ Gl?)
Field: En + L + V				
Tc + Ab	967	505	119	En + L (+ Fo?)
En + Ab + Q	950	810	23	En + L (+ Fo?)
Tc + Ab	925	995	93	En + L
En + Ab + Q	910	2000	1	En + L
Field: Fo + En + L + V				
Tc + Ab	1005	500	22	Fo + En + L
Curve: En + Ab + L + V				
Tc + Ab	945	500	187	En + Ab + L
Tc + Ab	882	990	112	En + Ab? + L
Tc + Ab	897	995	116	En + L (+ M)
En + Ab + Q	897	995	116	En + L (+ M)
Tc + Ab	869	1200	162	En + Ab + L (+ M)
Field: En + Ab + L + V				
Tc + Ab	924	515	97	En + Ab + L
Curve: En + Ab + Gl + L + V				
mix	851	995	163	En + Ab? + Gl + L
Tc + Ab	860	1015	103	En + Ab + L
mix	860	1015	103	En + Gl + L
Tc + Ab	870	1000	87	En + Ab + L
mix	870	1000	87	En + Ab? + L
Tc + Ab	860	1200	162	En + Ab + Gl? + L (+ M)
Tc + Ab	869	1200	162	En + Ab + L (+ M)
Field: En + Ab + Q + V				
Tc + Ab	913	1	24	En + Ab + Q
Tc + Ab	899	250	145	En + Ab + Q
Tc + Ab	875	400	911	En + Ab + Q
Field: En + Ab + Tr + V				
Tc + Ab	925	245	209	En + Ab + Tr? (+ Q)
Curve: En + Ab + Tr + L + V				
Tc + Ab	944	250	131	En + Ab + Tr (+ Q)
Tc + Ab	952	250	70	En + Ab + L (+ Fo?)

TABLE 8 (Continued)

Condensed Starting Material	Temp. in °C	P _{vapor} in bars	Duration in hours	Condensed Run Products
Curve: En + Ab + Q + L + V				
Tc + Ab	882	515	134	En + Ab + Q + L
mix	882	515	134	En + Ab + L
Tc + Ab	900	515	177	En + Ab + L
Results of Investigation of the Composition Na ₂ O · 3MgO · Al ₂ O ₃ · 9SiO ₂ with Excess Water				
En + Ab	850	800	307	En + Gl + L (+ Ab + M)
En + Ab	856	795	306	En + Gl + L? (+ Ab + M)
En + Ab	866	795	306	En + Ab

TABLE 9

X-ray powder data for metastable phase M compared with synthetic and natural montmorillonite

Synthetic Montmorillonite, (Saponite), Ames and Sand (1958)		Synthetic Montmorillonite, present study		Natural Montmorillonite, Nagelschmidt (1938)	
collapsed spacing		normal spacing			
Intensity	d in Å	Intensity	d in Å	Intensity	d in Å
10	12.3	>10	12.3	>10	15.3
2	6.15	1	6.1	1	7.6
4	4.58	2	4.58	1	5.01
5	3.10	7	3.04	1	4.60
4	2.63	2	2.64	9	3.00
3	2.53	4	2.50	1	2.61
1	2.34	—	—	1	2.47
1	2.295	2	2.30	1	2.41
1	2.067	1	2.08		

Intensities visually estimated.

s = strong.

vs = very strong.

with the formula Na_{0.33}Mg_{3.00}Al_{0.33}Si_{8.67}O₁₀(OH)₂ (i.e., saponite) decomposes above 740°C and below 780°C (Ames and Sand, 1958, table 1).

Sodic montmorillonite encountered in the present study is considered metastable because, on long runs, glaucophane slowly grows at its expense (fig. 1).

Location of Curves

Figures 3 and 4 are P_{vapor}-T plots of the data given in tables 7 and 8 respectively. In figure 4, location of the β quartz-tridymite transition was taken from Tuttle and England (1955). P_{vapor}-T locations of curves are presented in tables 10 and 11. Each curve has been located at temperatures slightly in excess of those for which the low-temperature assemblage was obtained. This method is based on the observation that although high-temperature assemblages may persist indefinitely at low temperatures, the converse phenomenon (crystal-

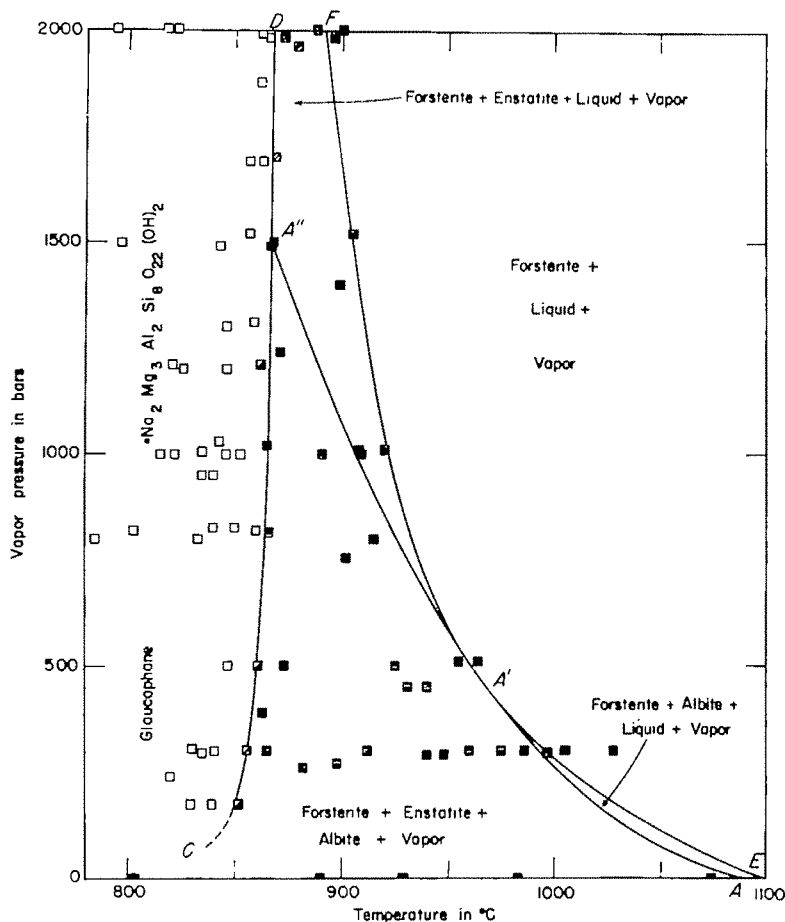


Fig. 3. P_{vapor} - T diagram for the composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 + \text{excess water}$. Divided run symbols indicate presence of the low-temperature assemblage in trace amounts. Curve locations at 1 atm (points A and E) were determined by Schairer and Yoder (1960, and personal communication).

lization of a mineral at temperatures in excess of its stability field) is rare, especially in the P_{vapor} - T range investigated.

Oxide mixtures, crystal assemblages, and in some cases glass were employed for the determination of each curve. It was found that oxide mixtures and glass for both investigated bulk compositions yielded melt at temperatures as much as 25° to 50°C lower than obtained using the assemblages forsterite + enstatite + albite, enstatite + albite + quartz, and talc + albite (all with or without glaucophane) previously crystallized from either glass or oxide mixtures. (See table 7, runs at 853°C and 1000 bars P_{vapor} , 843°C and 1490 bars P_{vapor} , 955°C and 510 bars P_{vapor} ; table 8, 792°C and 505 bars P_{vapor} .) Apparently metastable melt resulted from incomplete reaction.

Curves representing the high-temperature stability limit of glaucophane are believed accurate to within $\pm 5^\circ\text{C}$, as shown by reversals of the reaction

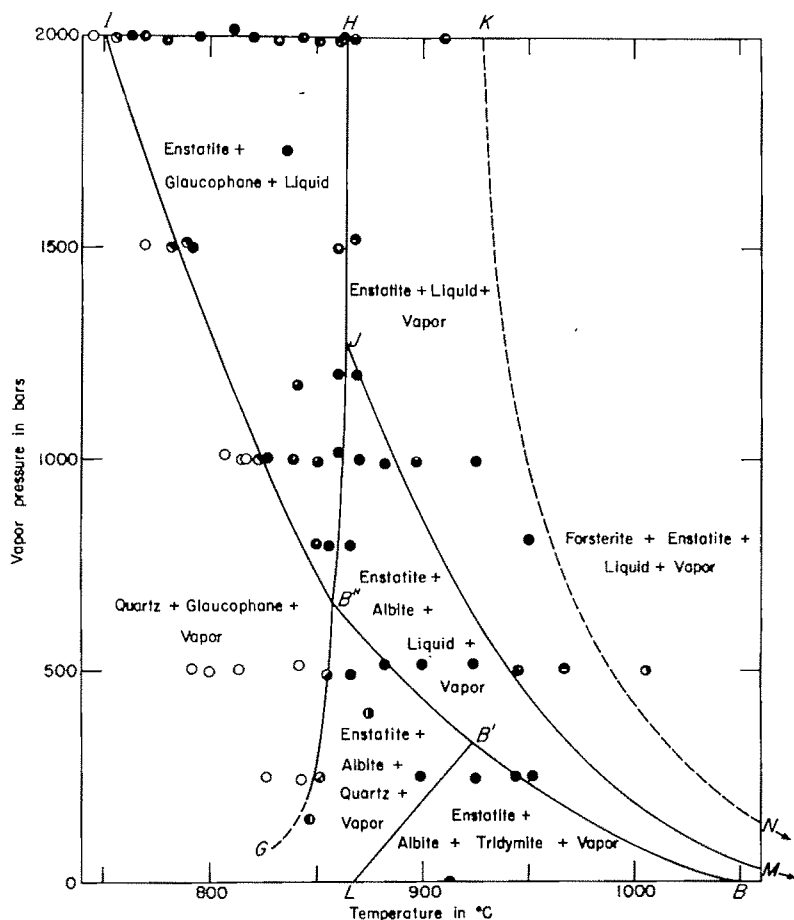


Fig. 4. P_{vapor} - T diagram for the composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 + \text{excess water}$. Divided run symbols indicate presence of the low-temperature assemblage in trace amounts. Curve locations at 1 atm (points B, M, and N) were determined by Schairer and Yoder (1960, and personal communication).

at 820 and 2000 bars vapor pressure for the bulk composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 + \text{excess water}$, and at 1500 bars vapor pressure for the bulk composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 + \text{excess water}$. Because the investigation was concerned primarily with amphibole stability, glaucophane field boundaries were determined with greater precision than were those involving equilibria exclusive of glaucophane. These latter curves are considered accurate to $\pm 10^\circ\text{C}$. For the bulk composition glaucophane + vapor, the melting curve of albite between 450 and 1500 bars vapor pressure is known with greater accuracy than is apparent from figure 3. The metastable extension of this curve into the glaucophane field was bracketed between 843° and 857°C at 2000 bars P_{vapor} , using the crystal assemblage forsterite + enstatite + albite (see table 7). Glaucophane grows very slowly from this assemblage, and, as it was not detected on these two runs, they are omitted from the phase diagram.

TABLE 10

P_{vapor}-T locations of curves presented in figure 3
(bulk composition Na₂O·3MgO·Al₂O₃·8SiO₂ + H₂O)

Curve	P _{vapor} (bars)	Temp. (°C)
Fo + En + Ab + Gl + V	175	850 ± 5
	300	855 ± 5
	500	859 ± 5
	820	863 ± 5
	1000	864 ± 5
	1300	866 ± 5
	1500	867 ± 5
Fo + En + Ab + L + V	1*	1093 ± 5
	300	993 ± 10
	(450)	(968 ± 10)
	500	961 ± 10
	1000	906 ± 10
	1500	867 ± 5
Fo + En + Gl + L + V	1500	867 ± 5
	1700	868 ± 5
	2000	868 ± 5
Fo + Ab + L + V	1*	1103 ± 5
	300	996 ± 10
	(450)	(968 ± 10)
Fo + En + L + V	(450)	(968 ± 10)
	500	961 ± 10
	1500	905 ± 10
	2000	892 ± 10

* Phase relations at atmospheric pressure determined by Schairer and Yoder (1960, and personal communication).
Parentheses enclose interpolated P-T values.

Stability of glaucophane in this P_{vapor}-T region is indicated by numerous runs in which it was obtained, and especially by the experiment at 862°C and 1990 bars P_{vapor}, in which glaucophane grew at the expense of the high-temperature equivalent assemblage. The melting curve of albite for the bulk composition quartz + glaucophane + vapor is known with greater accuracy than is apparent from figure 4. The metastable extension of this curve into the field enstatite + glaucophane + liquid was bracketed between 820° and 832°C at 2000 bars vapor pressure (see table 8).

Discussion of Phase Diagrams

To a good approximation, all phases obtained for the investigated bulk compositions fall within the quaternary system 2MgO·SiO₂-Na₂O·Al₂O₃·6SiO₂-SiO₂-H₂O. Any departure of the compositions of liquid and vapor from this system is so small as to produce no measurable change in properties or relative proportions of the crystals. The system 2MgO·SiO₂-Na₂O·Al₂O₃·6SiO₂-SiO₂-H₂O is shown diagrammatically in figure 5. Phase relations discussed below may be more clearly visualized by reference to this figure.

The shapes of glaucophane P_{vapor}-T fields are similar to those of other hydrous silicates, but the high-temperature stability limit of this mineral has a

TABLE 11

P_{vapor}-T locations of curves presented in figure 4
(bulk composition Na₂O·3MgO·Al₂O₃·10SiO₂ + H₂O)

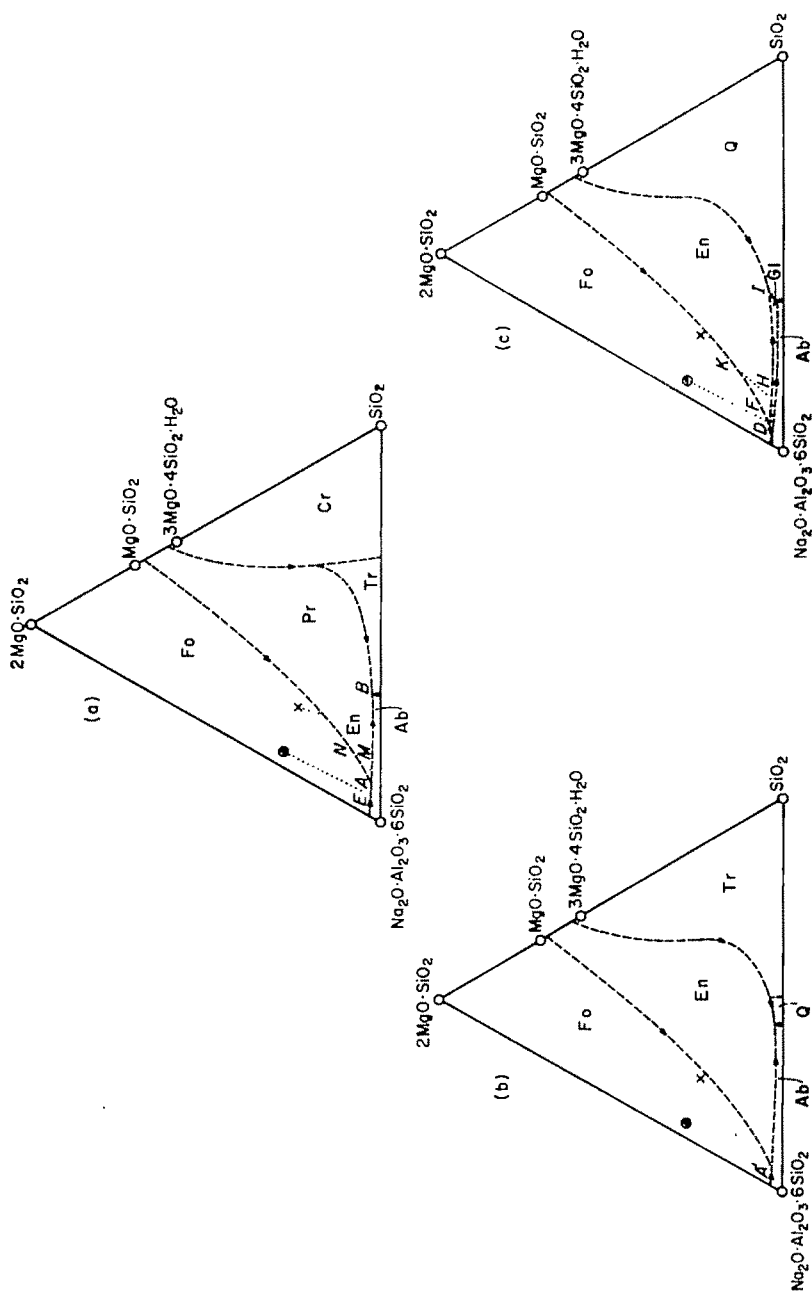
Curve	P _{vapor} (bars)	Temp. (°C)
En + Ab + Q + Gl + V	250	849 ± 5
	500	855 ± 5
	(660)	(857 ± 5)
En + Ab + Tr + L + V	1*	1050 ± 10
	250	946 ± 10
	(330)	(924 ± 10)
En + Ab + Q + L + V	(330)	(924 ± 10)
	500	887 ± 10
	(660)	(857 ± 5)
En + Q + Gl + L + V	(660)	(857 ± 5)
	1000	825 ± 5
	1500	785 ± 5
	2000	751 ± 5
En + Ab + Gl + L + V	(660)	(857 ± 5)
	800	859 ± 5
	1000	861 ± 5
	1200	863 ± 5
	(1280)	(863 ± 5)
En + Ab + L + V	1*	1103 ± 5
	500	941 ± 10
	1000	887 ± 10
	1200	870 ± 10
	(1280)	(864 ± 5)
En + Gl + L + V	(1280)	(864 ± 5)
	1500	864 ± 5
	2000	865 ± 5
Fo + En + L + V	1*	1152 ± 5
	500	990 ± 10

* Phase relations at atmospheric pressure determined by Schairer and Yoder (1960 and personal communication).

Parentheses enclose interpolated P-T values.

very steep dP/dT slope. An additional complexity appears in the phase diagram for the composition Na₂O·3MgO·Al₂O₃·10SiO₂ + excess water where glaucophane coexists with melt in a divariant region.

Fig. 5. Diagrammatic representation of liquidus surfaces in the system 2MgO·SiO₂-Na₂O·Al₂O₃·6SiO₂-SiO₂-H₂O at pressures of (a) 1 atm total pressure, (b) 450 bars P_{vapor}, and (c) 2000 bars P_{vapor}. The H₂O apex is towards the reader, and liquidus surfaces are projected onto the ternary face 2MgO·SiO₂-Na₂O·Al₂O₃·6SiO₂-SiO₂. Preliminary results obtained at 1 atm total pressure by Schairer and Yoder (1960, and personal communication) are the basis for 5a. Details of the protoenstatite-orthoenstatite inversion and location of the two-liquid region at high silica values have been omitted for simplicity. Liquidus relations at elevated vapor pressures are inferred from crystallization sequences and treatment of invariant points for the compositions Na₂O·3MgO·Al₂O₃·8SiO₂ + H₂O (indicated by +) and Na₂O·3MgO·Al₂O₃·10SiO₂ + H₂O (indicated by x). Glaucophane becomes stable in the presence of melt at 858°C and 660 bars P_{vapor} (fig. 4, point B''); with increasing vapor pressure, the primary crystallization field of amphibole expands and reaches the composition of the quaternary reaction point (fig. 3, point A'') at 867°C and 1500 bars.



wt per cent

Fig. 5

Glaucophane + vapor.—At low vapor pressures the high-temperature assemblage adjoining that of glaucophane consists of forsterite, enstatite, albite, and vapor. Schairer and Yoder (1960, and personal communication) determined the melting behavior at 1 atm for the composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ (points A and E in figs. 3 and 5a). They found that below $1093^\circ \pm 5^\circ\text{C}$ the stable assemblage for this bulk composition consists of forsterite, albite, and $\text{MgO} \cdot \text{SiO}_2$, between $1093^\circ \pm 5^\circ\text{C}$ and $1103^\circ \pm 5^\circ\text{C}$ of forsterite, albite, and liquid, and above $1103^\circ \pm 5^\circ\text{C}$ of forsterite and liquid. These authors place the ternary reaction point (A in figs. 3 and 5a) at $1098^\circ \pm 5^\circ\text{C}$ (personal communication) and the forsterite-albite binary eutectic at $1100^\circ \pm 5^\circ\text{C}$, so the temperatures of A and E in figure 3 are probably between 1093° and 1098°C and between 1098° and 1100° respectively. For this bulk composition, the melting curves of albite (EA') and enstatite (AA') become tangent (point A') at 968°C and 450 bars P_{vapor} ; with pressures in excess of this amount, albite melts at a lower temperature than enstatite. At 1500 bars P_{vapor} and 867°C (point A'') the albite melting curve (A'A'') intersects the high-temperature stability limit of glaucophane (CA'D); with greater vapor pressure forsterite, enstatite, liquid, and vapor are the high-temperature assemblage adjacent to the glaucophane field. A break in slope of the glaucophane field boundary must occur at the 1500 bar point since the two different reactions involving glaucophane should have different $\Delta S/\Delta V$ values; however, as figure 3 shows, within experimental limits of error, this discontinuity is undetectable.

The low-temperature melting curves (that of enstatite below 450 bars P_{vapor} , and that of albite at vapor pressures greater than 450 bars) represent the $P_{\text{vapor}}\text{-}T$ migration of the quaternary reaction liquid (melt in equilibrium with forsterite, enstatite, albite, and vapor) in the system $2\text{MgO} \cdot \text{SiO}_2\text{-Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2\text{-SiO}_2\text{-H}_2\text{O}$. This migration (curve AA'A'') must proceed along a smooth $P\text{-}T$ curve, independent of bulk composition. Although with increasing vapor pressure the binary eutectic between albite and silica is displaced towards the component SiO_2 , compared to the "dry" data (Tuttle and Bowen, 1958, p. 52), the composition of the quaternary reaction liquid must move towards the component $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ to produce the observed intersection of the melting curves of albite and enstatite (fig. 5). The simultaneous appearance of enstatite and albite in equilibrium with forsterite and liquid occurs at the vapor pressure where the composition of forsterite, the bulk composition, and quaternary reaction liquid (A') lie on a straight line in the ternary projection (fig. 5b). It is suggested that the peritectic between forsterite and enstatite retreats towards the $2\text{MgO} \cdot \text{SiO}_2$ apex at elevated vapor pressure, causing expansion of the primary crystallization field of enstatite. An alternative explanation is that the forsterite-enstatite field boundary does not change appreciably, but the eutectic between forsterite and albite migrates towards the $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ apex.

From figure 5 it is apparent that the contemporaneous beginning of crystallization of enstatite and albite in the presence of forsterite will occur at a specific vapor pressure and temperature for a particular bulk composition. For a composition richer in silica than $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$, this point lies on the $P_{\text{vapor}}\text{-}T$ curve for the quaternary reaction liquid at a vapor pressure

less than 450 bars. The described intersection of P-T curves is a point on a univariant P-T-x curve (not shown in figure 3) along which the five phases forsterite, enstatite, albite, liquid, and vapor coexist. The single degree of freedom (five phases present in a four-component system) indicates that for a range of bulk compositions, and therefore a range of vapor pressures, the crystallization path proceeds through the forsterite field directly to the location of the quaternary reaction liquid, where enstatite and albite simultaneously become stable.

Quartz + glaucophane + vapor.—At low vapor pressures the high-temperature assemblage adjoining that of quartz + glaucophane + vapor consists of enstatite, albite, quartz, and vapor. Schairer and Yoder (1960, and personal communication) determined liquidus-solidus relations for the composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$ at atmospheric pressure (points B, M, and N in figs. 4 and 5a) and found that below $1050^\circ \pm 10^\circ\text{C}$ the stable assemblage consists of enstatite, albite, and tridymite; between $1050^\circ \pm 10^\circ\text{C}$ and $1103^\circ \pm 5^\circ\text{C}$, of enstatite, albite, and liquid; between $1103^\circ \pm 5^\circ\text{C}$ and $1152^\circ \pm 5^\circ\text{C}$, of $\text{MgO} \cdot \text{SiO}_2$ and liquid; and above $1152^\circ \pm 5^\circ\text{C}$, of forsterite + $\text{MgO} \cdot \text{SiO}_2$ + liquid. The 1 atm melting relations quoted are the actual temperature values obtained by Schairer and Yoder for the bulk compositions $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$. Inspection of figure 5a indicates that the liquidus temperature of point E must exceed that of A which in turn has a value higher than that of M.

As shown in figure 5, with decreasing temperature crystallization commences with forsterite, joined at slightly lower temperatures by $\text{MgO} \cdot \text{SiO}_2$. The quaternary reaction point (in projection) lies to the left of the extension of the join connecting $\text{MgO} \cdot \text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$. Thus, as heat is subtracted from the system, forsterite reacts with melt to form additional enstatite and is completely used up as the liquid reaches the composition N (at 1 atm total pressure), or K (at 2000 bars P_{vapor}). On further cooling, the liquid leaves the forsterite field boundary and moves through the primary field of crystallization of enstatite directly away from the composition $\text{MgO} \cdot \text{SiO}_2$ to the junction with the albite field boundary (M in fig. 5a) or the primary field of crystallization of glaucophane (H in fig. 5c). The migration of the liquid through the enstatite field is indicated in figure 4 by the assemblage enstatite + liquid + vapor.

The eutectic in the system $2\text{MgO} \cdot \text{SiO}_2$ - $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ - 6SiO_2 - SiO_2 -(H₂O) is at point B in figure 5a; liquid of this composition is in equilibrium with enstatite, albite, a silica mineral (and vapor). The P_{vapor} -T migration of this minimum is shown in figure 4 as curve BB'B''. At 924°C and 330 bars vapor pressure (point B') this curve intersects the curve for the β quartz-tridymite transition. Because of differences in volumes and entropies of these two latter phases, the minimum melting curve should exhibit a discontinuity in slope, but as indicated in figure 4 the inflection is slight.

The minimum melting curve intersects the high-temperature stability limit of glaucophane at 857°C and 660 bars P_{vapor} (point B''). Treatment of this point (see section on invariant points and fig. 7) indicates that the high-temperature amphibole stability limit below 660 bars P_{vapor} (curve GB'') has

a steeper dP/dT slope than the glaucophane boundary at vapor pressures in excess of this amount (curve B''J). Qualitatively this inflection may be visualized by consideration of reactions involved. Curve GB'' defines the univariant curve for the reaction (1) $Q + Gl \rightarrow En + Ab + V$, and curve B''J, the reaction (2) $Gl + L \rightarrow En + Ab + V$. Only phases taking part in the reactions are specified. Products in both reactions are the same phases. The reactants in (2) are more hydrous than those of (1). Hence because of the evolution of vapor, $\Delta V_{Gl + L \rightarrow En + Ab + V}$ is greater than $\Delta V_{Q + Gl \rightarrow En + Ab + V}$. Reaction (2) proceeds with a smaller ΔS than (1) because entropy of the liquid is greater than that of quartz. Therefore, the curve defining the high-temperature stability limit of glaucophane above 660 bars P_{vapor} must have a smaller value of $\Delta S/\Delta V$, and hence a more gentle dP/dT slope than that of the curve below 660 bars.

At temperatures in excess of curve B''J, albite + enstatite are stable in the presence of vapor. However, below this curve all the albite and part of the enstatite react with vapor to produce glaucophane and small amounts of melt. This unusual behavior is verified by experiments performed on the composition $Na_2O \cdot 3MgO \cdot Al_2O_3 \cdot 9SiO_2 + \text{excess } H_2O$ (enstatite + albite + vapor). Run data are presented at the end of table 8. At still lower temperatures (below curve B''I) quartz, additional glaucophane, and vapor are produced at the expense of all the remaining enstatite and liquid.

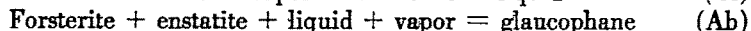
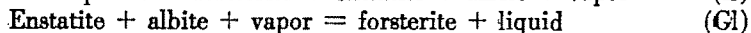
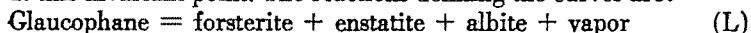
Intersection of the albite melting curve with the high-temperature glaucophane stability limit at 863°C, 1280 bars P_{vapor} (point J in fig. 4) gives rise to another inflection in the amphibole boundary due to differences in ΔV and ΔS for reactions involving glaucophane. At vapor pressures in excess of this intersection, the high-temperature stability limit of glaucophane (JH) has a nearly vertical dP/dT slope, as indicated in figure 4.

THERMODYNAMIC CONSIDERATIONS

Application of Phase Theory to Glaucophane P_{vapor} -T Curves

Glaucophane + vapor.—Experimental investigation of the composition $Na_2O \cdot 3MgO \cdot Al_2O_3 \cdot 8SiO_2$ with excess water located an invariant point in the system $2MgO \cdot SiO_2 - Na_2O \cdot Al_2O_3 \cdot 6SiO_2 - SiO_2 - H_2O$ at 867°C and 1500 bars, where forsterite, enstatite, albite, glaucophane, liquid, and vapor coexist. The anhydrous composition of the liquid was determined utilizing the crystallization sequence obtained in this study together with data on the ternary system $2MgO \cdot SiO_2 - Na_2O \cdot Al_2O_3 \cdot 6SiO_2 - SiO_2$ (Schairer and Yoder, 1960, and personal communication). Water content of the liquid, 5 ± 2 weight percent, was determined by dehydrating glass quenched from the conditions $P_{\text{vapor}} = 1500$ bars, $T = 868^\circ\text{C}$. The vapor was assumed to be nearly pure H_2O , inasmuch as glass droplets (which would result from condensation of a silica-rich vapor) were never observed.

Six univariant curves, along each of which five phases are stable, terminate at this invariant point. The reactions defining the curves are:



Forsterite + liquid + vapor = albite + glaucophane (En)

Forsterite + liquid = enstatite + albite + glaucophane (V)

Glaucophane + liquid = enstatite + albite + vapor (Fo)

These reactions were obtained by constructing joins and three-phase triangles within the tetrahedron $2\text{MgO} \cdot \text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{SiO}_2 - \text{H}_2\text{O}$, and checked using algebraic and graphical methods described by Niggli (1954, p. 403-411). Each curve is designated by enclosing in parentheses the symbol for the phase which does not take part in the reaction. Only three of these curves

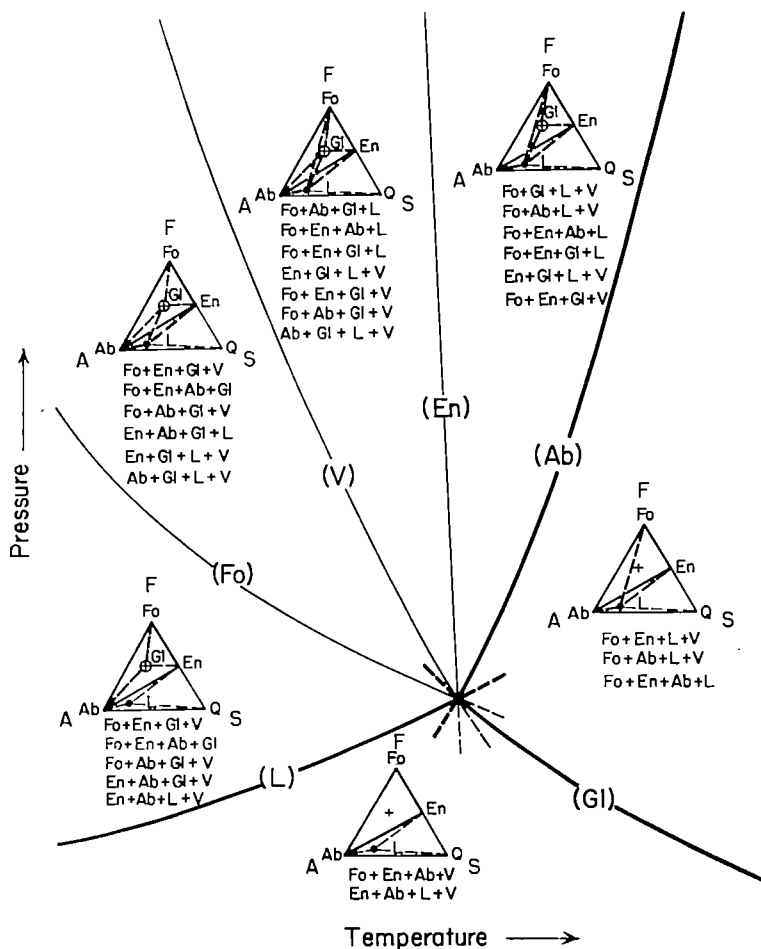


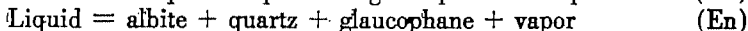
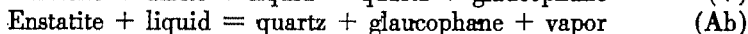
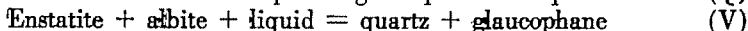
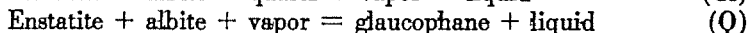
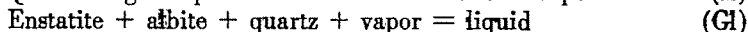
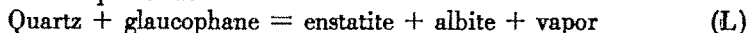
Fig. 6. Schematic arrangement of all possible curves that terminate at the invariant $\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ -point at 867°C , 1500 bars vapor pressure, in the system $2\text{MgO} \cdot \text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{SiO}_2 - \text{H}_2\text{O}$. Diagrammatic tetrahedra (in mole percent) indicate phase compatibilities between curves. Heavy joins and listed assemblages are appropriate for the subsystem undersaturated with respect to silica. Solid joins lie on the plane $2\text{MgO} \cdot \text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{SiO}_2$; dashed joins lie within the quaternary system $2\text{MgO} \cdot \text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{SiO}_2 - \text{H}_2\text{O}$. Joins with vapor have been omitted.

are shown in figure 3, because changes of bulk composition are necessary to obtain (Fo) and (En) experimentally, and (V) can be realized only by exclusion of the vapor phase (prohibited by the experimental technique). The coincidence theorem of Morey and Williamson (1918) indicates that curve (En) lies between (V) and (Ab), curve (Fo) lies between (L) and (V), and that one or more curves lie between (Fo) and (Gl). In figure 6 the arrangement of all possible curves is presented schematically.

Tetrahedra (also shown diagrammatically in mole percent for clarity) for the system $2\text{MgO} \cdot \text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{SiO}_2 - \text{H}_2\text{O}$ with water-bearing phases projected onto the plane of the paper ($2\text{MgO} \cdot \text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{SiO}_2$) indicate phase relations between the curves. All phases considered (except liquid) lie within the subsystem $2\text{MgO} \cdot \text{SiO}_2 - \text{MgO} \cdot \text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{H}_2\text{O}$. Silica-saturated assemblages are indicated by lighter lines. Solid joins lie on the ternary face $2\text{MgO} \cdot \text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{SiO}_2$; broken tie lines lie within the tetrahedron. Joins with the H_2O apex are not shown. With or without vapor, glaucophane is stable in all areas at lower temperature than curve (Ab) and at higher pressure than curve (L). In addition to the projected tetrahedra, figure 6 lists all possible phase assemblages within the "subsystem" undersaturated with respect to silica for each P-T field.

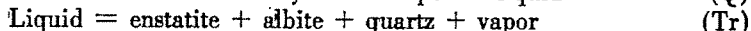
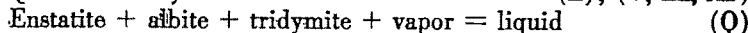
Quartz + glaucophane + vapor.—Experimental investigation of the composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$ with excess water located two more invariant points in the system $2\text{MgO} \cdot \text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{SiO}_2 - \text{H}_2\text{O}$, one at 857°C and 660 bars, where enstatite, albite, quartz, glaucophane, liquid, and vapor are stable, the other at 924°C and 330 bars, where enstatite, albite, quartz, tridymite, liquid, and vapor coexist. Dehydration of glass quenched from the conditions $P_{\text{vapor}} = 1000$ bars, $T = 870^\circ\text{C}$, yields a value of approximately 6 ± 3 weight percent H_2O . Treatment of these invariant points was carried out as described above.

The six curves which intersect at 857°C and 660 bars are defined by the univariant equilibria:



The arrangement of these curves is presented diagrammatically in figure 7. Pure glaucophane is stable in all six fields, but for the investigated bulk composition, $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 + \text{H}_2\text{O}$, amphibole is confined to the P-T region where temperatures are less than those of curve (Q), and pressures are in excess of curve (L). Silica-saturated assemblages are indicated by heavy lines and are listed between the univariant curves.

The invariant point at 924°C and 330 bars represents the intersection of three curves indicated by the univariant reactions:



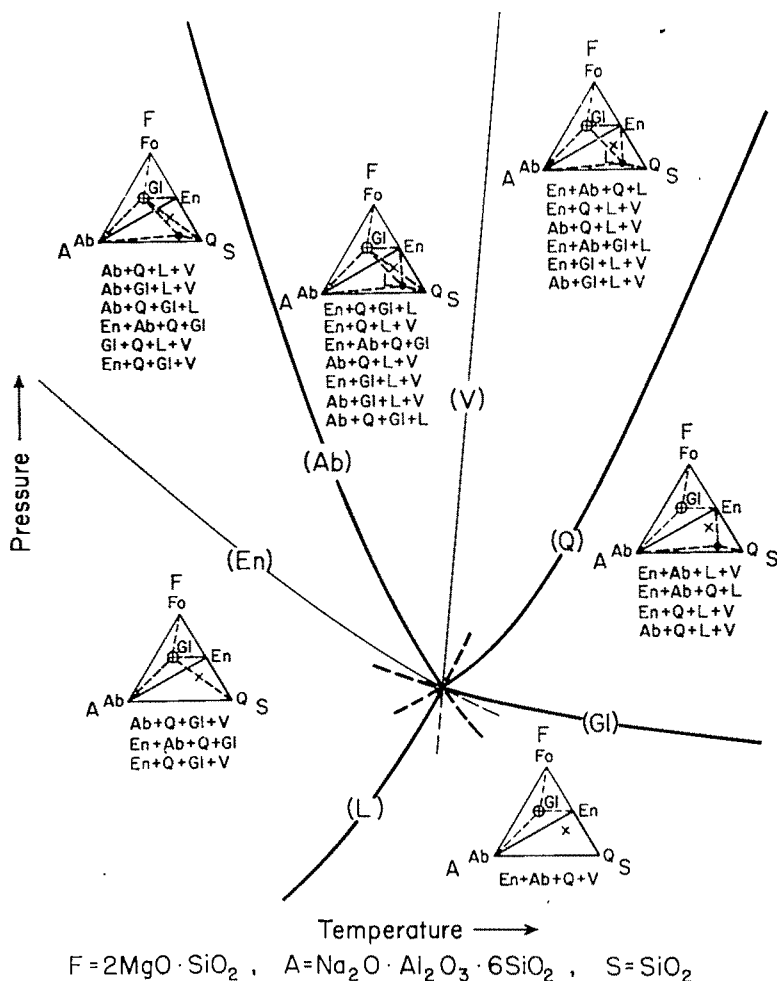


Fig. 7. Schematic arrangement of all possible curves that terminate at the invariant point at 858°C, 660 bars vapor pressure in the system $2MgO \cdot SiO_2 - Na_2O \cdot Al_2O_3 \cdot 6SiO_2 - SiO_2 - H_2O$. Diagrammatic tetrahedra (in mole percent) indicate phase compatibilities between curves. Heavy joins and listed assemblages are appropriate for the subsystem super-saturated with respect to silica. Solid joins lie on the plane $2MgO \cdot SiO_2 - Na_2O \cdot Al_2O_3 \cdot 6SiO_2 - SiO_2$; dashed joins lie within the quaternary system $2MgO \cdot SiO_2 - Na_2O \cdot Al_2O_3 \cdot 6SiO_2 - SiO_2 - H_2O$. Joins with vapor have been omitted.

This is a case of triple degeneracy (Niggli, 1954, p. 387-391), resulting from the coincidence of curves (V), (En), and (Ab) with the metastable extension of curve (L). Degeneracy occurs because one of the univariant curves ($Q = Tr$) is a polymorphic transition, all other phases being indifferent (Morey and Williamson, 1918). A schematic representation of these curves is presented in figure 8. As in figure 7, assemblages appropriate to the "subsystem" super-saturated with respect to silica are shown in heavy lines and are listed between the curves.

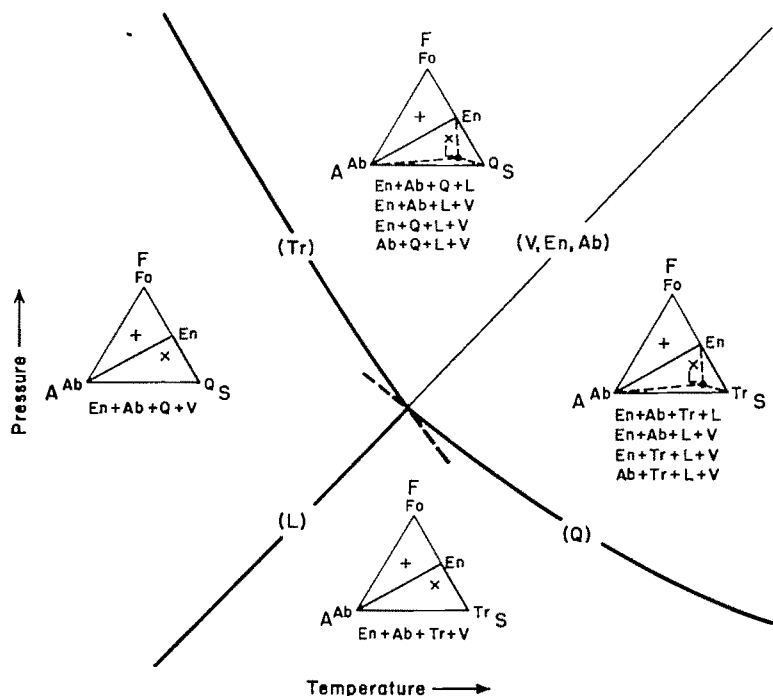


Fig. 8. Schematic arrangement of all possible curves that terminate at the degenerate invariant point at 924°C, 330 bars vapor pressure in the system $2MgO \cdot SiO_2 - Na_2O \cdot Al_2O_3 \cdot 6SiO_2 - SiO_2 - H_2O$. Diagrammatic tetrahedra (in mole percent) indicate phase compatibilities between curves. Heavy joins and listed assemblages are appropriate for the subsystem supersaturated with respect to silica. Solid joins lie on the plane $2MgO \cdot SiO_2 - Na_2O \cdot Al_2O_3 \cdot 6SiO_2 - SiO_2$; dashed joins lie within the quaternary system $2MgO \cdot SiO_2 - Na_2O \cdot Al_2O_3 \cdot 6SiO_2 - SiO_2 - H_2O$. Joins with vapor have been omitted.

Discussion of the Primary Crystallization Field of Glaucophane

Treatment of the non-degenerate invariant points (figs. 6 and 7) yields information concerning glaucophane primary crystallization field boundaries diagrammatically illustrated in figure 5c. For the bulk compositions $Na_2O \cdot 3MgO \cdot Al_2O_3 \cdot 8SiO_2 + \text{excess } H_2O$ and $Na_2O \cdot 3MgO \cdot Al_2O_3 \cdot 10SiO_2 + \text{excess } H_2O$, glaucophane + liquid + vapor can coexist with either albite or enstatite, but not both; hence the primary crystallization field of glaucophane must lie between those of the other two phases. Glaucophane first appears on the liquidus surface at the quaternary minimum (point B'' in fig. 4) at 857°C and 660 bars P_{vapor} , and its primary field of crystallization expands with increased pressure until at 867°C and 1500 bars P_{vapor} it reaches the composition of the quaternary reaction liquid (point A'' in fig. 3). At higher vapor pressures, say 2000 bars, the field boundary between forsterite and glaucophane must decline in temperature proceeding from the junction with the primary field of crystallization of enstatite (point D in fig. 5c) towards albite. This situation is indicated in figure 6 by curves (En) and (Ab); the former, along which the

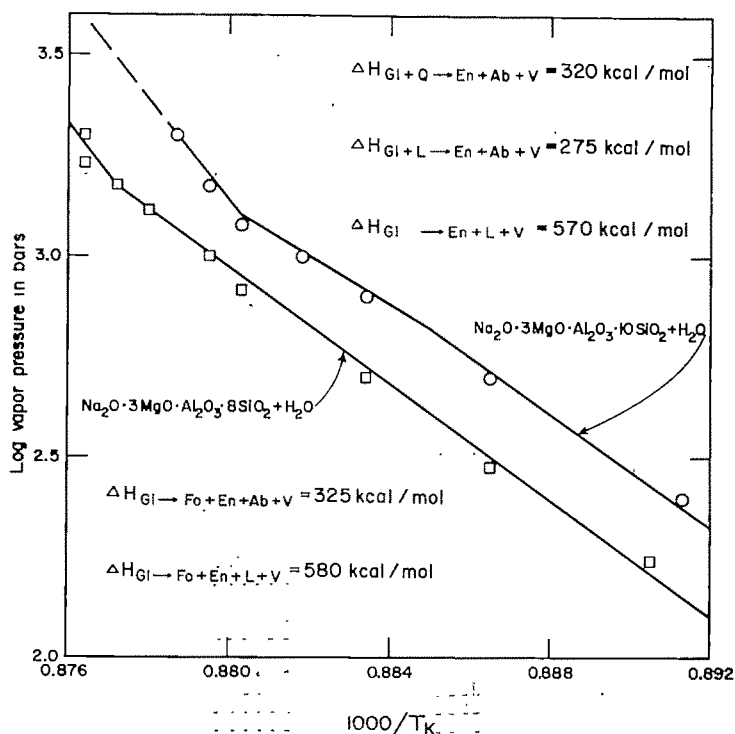


Fig. 9. Stability field of glaucophane plotted against $\log P_{\text{vapor}}$ and $1/T_K$. Squares indicate curve locations for the bulk composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 + \text{excess H}_2\text{O}$; circles indicate curve locations for the bulk composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 + \text{excess H}_2\text{O}$.

phases forsterite + albite + glaucophane + liquid + vapor coexist, lies at a lower temperature than the latter, along which forsterite + enstatite + glaucophane + liquid + vapor are stable. The temperatures of the field boundaries between enstatite and glaucophane, and between albite and glaucophane must diminish towards the SiO_2 apex, as shown by the experimental results. The field boundary between quartz and glaucophane must decrease in temperature from the primary crystallization field of enstatite (point I in fig. 5c) towards the $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{SiO}_2 - \text{H}_2\text{O}$ side face as indicated by fig. 7: glaucophane + liquid + vapor coexist with albite at temperatures as low as curve (En), although at higher temperatures glaucophane + liquid + vapor is in stable equilibrium with enstatite only above curve (Ab).

ΔH and ΔS for Reactions Involving Glaucophane

Glaucophane + vapor.—The decomposition curve of a volatile-bearing mineral may closely approach a straight line plotted against $\log P_{\text{vapor}}$ and

$1/T_K$; the slope of this line is $-\frac{\Delta H}{2.303R}$, where R is the universal gas constant.

Such treatment assumes that the vapor behaves as an ideal gas, the heat of the reaction is independent of temperature, and the volume change of reacting

condensed phases is negligible. Curves bounding the glaucophane stability field plotted against $\log P_{\text{vapor}}$ and $1/T_K$, and derived values of ΔH are presented in figure 9. Dehydration of glaucophane requires approximately half the heat consumed by its incongruent melting at higher pressures.

The ΔH value of 325 kilocalories per mole for the breakdown of glaucophane to forsterite, enstatite, albite, and vapor determined by this method can be checked by calculation using the Clapeyron equation. The molar volume of synthetic glaucophane was computed from unit cell dimensions determined in this study. Molar volumes for the other phases were taken from Fairbairn (1943, table 4) and Holser and Kennedy (1959). Calculated enthalpies and entropy changes for three different points on the curve $\text{Fo} + \text{En} + \text{Ab} + \text{Gl} + \text{V}$ are:

$\Delta H = 315 \text{ kcal/mol}$, $\Delta S = 275 \text{ cal/mol/deg}$, at 859°C , 500 bars P_{vapor} ;

$\Delta H = 330 \text{ kcal/mol}$, $\Delta S = 290 \text{ cal/mol/deg}$, at 864°C , 1000 bars P_{vapor} ;

$\Delta H = 340 \text{ kcal/mol}$, $\Delta S = 300 \text{ cal/mol/deg}$, at 867°C , 1500 bars P_{vapor} .

In this calculation it was assumed that the volume change of the solids is independent of temperature and pressure. It should be pointed out that evaluation of ΔH by this method depends on accurate determination of the curve slope; as can be seen from figure 3, the relative pressure insensitivity of the glaucophane stability limit prohibits accurate measurement of dP/dT .

In spite of rather large limits of error, both the integrated Clausius-Clapeyron graphical solution and the Clapeyron equation yield the same heat of reaction, $330 \pm 60 \text{ kcal/mol}$. This value is almost an order of magnitude larger than those for most silicate dehydrations (see Ernst, 1960, table 10).

The entropy of glaucophane at 864°C and 1000 bars vapor pressure, $150 \pm 50 \text{ cal/mol/deg}$, was obtained by subtracting the entropy change for the reaction $\text{glaucophane} = \text{forsterite} + \text{enstatite} + \text{albite} + \text{vapor}$ ($290 \pm 50 \text{ cal/deg/mol}$) from the total entropy of the assemblage $\text{forsterite} + \text{enstatite} + \text{albite} + \text{vapor}$. Thermochemical data and sources are listed in table 12.

The change in coordination of aluminum from octahedral in glaucophane to tetrahedral in albite can account for only a portion of the enthalpy and entropy change involved in the decomposition of glaucophane. Reasons for the extreme values reported here are not known. Small errors in curve location would introduce large changes in ΔH and ΔS , but it is clear from this investigation that the entropy and enthalpy of glaucophane are unusually low compared to other silicates.

Quartz + glaucophane + vapor.—The addition of SiO_2 depresses the high-temperature stability limit of glaucophane because the Gibbs free energy of the high-temperature assemblage is lowered (reflecting the conversion of forsterite to enstatite) relative to the free energy of glaucophane (which is silica-saturated) + quartz.

Comparison of tables 10 and 11 indicates this effect is geologically insignificant, the temperature drop of the glaucophane stability limit being only 3° to 6°C . Moreover, since dP/dT slopes are practically parallel for glaucophane with and without quartz, calculated values of ΔH and ΔS for quartz + glaucophane reactions are nearly identical to those described above for pure glaucophane. For the reaction $\text{quartz} + \text{glaucophane} \rightarrow \text{enstatite} + \text{albite} +$

TABLE 12
Entropy data and sources

Compound	$S_{298}^{\circ K}$ (cal/deg/mol)	$V_{298}^{\circ K}$ (cc)	ΔS 1187-298°K (cal/deg/mol)	$V_{1187}^{\circ K}$ (cc)	$S_{1187}^{\circ K}$ (cal/deg/mol)
H ₂ O (solid)	9.4 (7)	13.7	—	—	—
" (liquid)	16.75 (3)	18.0	—	—	—
" (vapor)	—	—	40.25 (3)*	87.5†	57.0* 43.1†
MgO	6.55 (3)	11.2	—	—	—
MgO·H ₂ O	15.1 (1)	24.3	—	—	—
MgO·SiO ₂	16.22 (3)	31.5	33.6 (2)	same	49.8
2MgO·SiO ₂	22.75 (3)	43.8	48.6 (5)	same	71.35
3MgO·4SiO ₂ ·H ₂ O	62.3 (6)	131.1	—	—	—
3MgO·2SiO ₂ ·2H ₂ O	56 (9)	101	—	—	—
7MgO·8SiO ₂ ·H ₂ O	130 (9)	263	—	—	—
Na ₂ O·Al ₂ O ₃ ·6SiO ₂	100.4 (4)	202	172.9 (4)	same	273.3
Na ₂ O·Al ₂ O ₃ ·4SiO ₂	63.8 (4)	121.4	—	—	—
Na ₂ O·3MgO·Al ₂ O ₃ · 8SiO ₂ ·H ₂ O	136 (8)	270	—	same	147.5
SiO ₂	10.00 (3)	22.6	20.07 (2)	same	30.07

(1) Glaue and Archibald, 1937.

(2) Kelley, 1949.

(3) Kelley, 1950.

(4) Kelley and others, 1953.

(5) Orr, 1953.

(6) Robie, 1957.

(7) Fyfe and others, 1958, p. 31.

(8) $\Sigma S_{298}^{\circ K} + S_{298}^{\circ K} + S_{298}^{\circ K} + S_{298}^{\circ K} + S_{298}^{\circ K}$ and including volume correction (Fyfe and others, 1958, p. 28-34).

(9) $\Sigma S_{298}^{\circ K}$ and including volume correction (Fyfe and others, 1958, p. 28-34).

* 1 atm pressure.

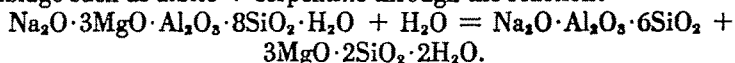
† 1000 bars pressure.

vapor, the integrated Clausius-Clapeyron graphical solution (fig. 9) gives a heat of reaction of 320 kcal/mol; measurement of the curve slope at 855°C and 500 bars P_{vapor} yields a value of 325 kcal/mol for ΔH and 285 cal/mol/deg for ΔS . These computations are consistent with values derived for pure glaucophane and with published thermochemical data; silica saturation ($\text{Mg}_2\text{SiO}_4 + \text{SiO}_2 = 2\text{MgSiO}_3$) lowers the enthalpy of the high-temperature assemblage 7 kilocalories and the entropy 6 calories relative to the low-temperature assemblage as indicated in table 12.

DISCUSSION OF THE LOW-TEMPERATURE STABILITY LIMIT OF GLAUCOPHANE

Experiments on the composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 + \text{excess H}_2\text{O}$ indicate that glaucophane is stable at temperatures at least as low as 602°C at 2500 bars vapor pressure (table 7). A run at 377°C and 4650 bars P_{vapor} yielded albite + sodic montmorillonite; at such temperatures, reaction rates are low and equilibrium may not have been attained. If glaucophane does have

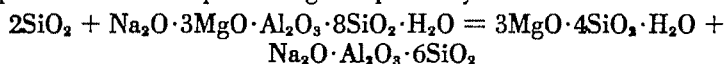
a low-temperature stability limit, it is probably replaced by a more hydrous assemblage such as albite + serpentine through the reaction:



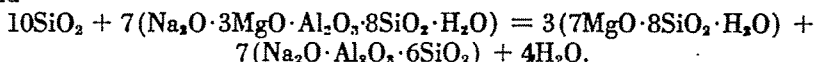
At 25°C and 1 atm total pressure, the reactants constitute the small volume, small entropy assemblage (table 12). Above 100°C, due to the vaporization of water at low pressures, they have a larger total volume and entropy than albite + serpentine. It is therefore possible that at some temperatures between the serpentine dehydration curve (Bowen and Tuttle, 1949, p. 447) and the liquid-vapor transition of water there exists a P-T region of stability for albite + serpentine. This field would pinch out at high pressures because of the rapid decrease in entropy and volume of the water. Above approximately 1000 bars P_{vapor} , glaucophane + water constitutes the low volume as well as the low entropy assemblage for all temperatures considered. Due to its low entropy and volume the stability of glaucophane will be almost unaffected by the partial pressure of water, but that of the assemblage albite + serpentine should be strongly influenced since its presumed stability results from the large entropy and volume of H_2O at low pressures. Therefore, compatibility of albite + serpentine (if possible at all) is favored by conditions in which vapor pressure approximates total pressure; a decrease in the ratio $P_{\text{vapor}}/P_{\text{total}}$ would favor expansion of the glaucophane + vapor P-T field at the expense of albite + serpentine.

The association of albitite dikes with serpentinites has been reported from glaucophane schist terrains (e.g., California, Turner, 1896, p. 380; Japan, J. Suzuki and Y. Suzuki, 1959, p. 366-368) but it is not clear if albite and serpentine are in equilibrium. An albitite dike-serpentine contact at Chester, Massachusetts, shown the writer by D. R. Wones, U. S. Geological Survey, displays a chlorite screen between the two rock types; hence the bulk composition of the contact zone is not equivalent to that of glaucophane (and albite + serpentine). Similarly, inclusions of albite-bearing rocks in serpentinites, and ultrabasic-graywacke contacts described from California commonly exhibit nodules or a contact selvage of actinolite + talc or actinolite + chlorite (Taliaferro, 1943, p. 150-181; Brothers, 1954, p. 622). In summary, although entropy-volume relations suggest the *possibility* of a P_{vapor} -T stability field for the assemblage albite + serpentine, neither experimental nor field data have yielded positive evidence of such a compatibility.

Laboratory investigation on the composition $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$ + excess water indicates that glaucophane can coexist with quartz at temperatures at least as low as 702°C at 2020 bars vapor pressure (table 8). Assemblages of equivalent bulk composition, talc + albite and anthophyllite + albite + vapor are related to quartz + glaucophane by the reactions:



and



The left side of each expression constitutes the small volume, small entropy

assemblage (table 12) and should be stable at low temperatures. Inasmuch as quartz and glaucophane are in equilibrium at high temperatures as well, as indicated by the experimental investigation, albite should be incompatible with either talc or anthophyllite.

Rabbitt (1948, table 13) has listed a number of assemblages where anthophyllite is associated with sodic plagioclase, and Stillwell and Edwards (1951) have described an occurrence of talc with albite in South Australia. These associations are puzzling but they are rare compared to the abundantly described and well-documented quartz + glaucophane assemblages typical of certain low-grade metagraywackes and metacherts (e.g., California, Taliaferro, 1943; Bloxam, 1959; Japan, Suzuki, 1930).

GEOLOGIC APPLICATION

Neither high pressure nor differential stress is required for the stable existence of glaucophane. Under appropriate chemical conditions, glaucophane is stable at magmatic temperatures; however, its absence as a primary constituent of igneous rocks attests to the fact that magmas do not satisfy such chemical requirements. By analogy with the experimentally investigated bulk compositions, $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 + \text{H}_2\text{O}$, and $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 + \text{H}_2\text{O}$, glaucophane should be stable over a wide P-T range in lime-deficient rocks which are rich in soda and magnesia relative to alumina; moreover, the presence of Na_2O in excess of Al_2O_3 in some rocks should favor crystallization of intermediate members of the glaucophane-riebeckite series (crossites). Because of the scarcity of such chemical environments, occurrences of glaucophane over a wide range of physical conditions are rare. Possible examples of low-grade glaucophane- and crossite-bearing rocks of unusual bulk composition are presented in table 13. Chemically these rocks roughly correspond to spilites but are associated with glaucophane schists of more "nor-

TABLE 13

Glaucophane schists characterized by high Na_2O , low CaO contents

Wt. percent	1	2	3	4
SiO_2	54.65	51.95	52.94	52.64
TiO_2	2.99	2.67	2.20	2.11
Al_2O_3	12.52	13.14	10.99	13.87
Fe_2O_3	5.55	5.59	3.61	4.48
FeO	5.97	7.58	9.56	6.83
MnO	0.15	0.09	0.14	0.08
MgO	5.32	7.08	7.28	8.28
CaO	3.87	2.58	2.23	1.98
Na_2O	6.30	5.46	7.08	6.08
K_2O	0.21	1.01	1.14	0.99
H_2O^+	2.15	2.36	2.30	2.53
P_2O_5	0.36	—	0.30	0.24
CO_2	—	—	—	—
Total	100.04	99.51	99.57	100.11

1 Chlorite-rich albite-crossite from Corsica (Brouwer and Egeler, 1952, p. 34).

2 Albite-glaucophane schist from Switzerland (Niggli and others, 1930, p. 174).

3 Glaucophane schist from Switzerland (Niggli and others, 1930, p. 174).

4 Glaucophane (sericite-chlorite) schist from Switzerland (de Quervain and Friedlaender, 1942, p. 16).

mal" composition (low Na_2O , high CaO contents). Although high-grade glaucophane-bearing rocks of unusual bulk composition are theoretically possible, this author is unaware of any such occurrences.

Many glaucophane schists have compositions indistinguishable from typical greenschists and epidote amphibolites. Provided they represent equilibrium assemblages, these glaucophane schists must have formed under P-T conditions different from those of greenschists and epidote amphibolites of similar chemical composition. The problem of the glaucophane schist facies will be discussed more fully in a forthcoming paper.

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LATE- AND POSTGLACIAL VEGETATIONAL HISTORY IN WISCONSIN, PARTICULARLY CHANGES ASSOCIATED WITH THE VALDERS READVANCE

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ABSTRACT. Late-glacial and postglacial sediments at three sites in central and eastern Wisconsin illustrate the effects of the Valders Readvance on the vegetation outside the Valders maximum. A *Picea* forest occupied the region on the retreat of the Cary ice during the Two Creeks Interval. During the Valders Readvance a *Picea* woodland with openings grew beyond the edge of the ice sheet. On the retreat of the Valders ice *Picea* forest reoccupied the region outside the Valders maximum, and the *Picea* woodland with openings invaded the area vacated by the ice. The forest succession in both areas is then through a *Pinus*-dominant phase to zones with hardwoods.

The climate of the late-glacial and its vegetation were more continental in the Midwest than in eastern North America and Northwest Europe.

INTRODUCTION

The primary aim of the investigations described here was to find whether or not there was any correlation between late-glacial¹ vegetational changes and the Valders Readvance² in its type area in Wisconsin. The results of such a correlation would obviously be of importance for the reconstruction of periglacial vegetational conditions. To this end pollen-analytical studies were made of sediment series from three sites, whose positions are shown in figure 1:

1. A bog in a kettle in a Cary end moraine 10 miles outside the mapped limit of the Valders (Red) Drift in Green Lake County; this is Disterhaft's Farm Bog, 4 miles southeast of Neshkoro.

2. A lake contained in an enclosed hollow in Valders Till; this is Seidel Lake, 1 mile southwest of Kewaunee, in the county of the same name.

3. The Two Creeks Forest Bed, between the Cary and Valders Drifts on the shores of Lake Michigan, 9 miles south of Kewaunee.

The expected theoretical relation among these three is sketched in figure 2. It would be expected that the sediments in the Cary kettle would cover Two Creeks, Valders, and postglacial time, whereas the sediments on the Valders Till would record postglacial time only. Because of the paucity of pollen evidence from the Two Creeks Forest Bed, a reinvestigation of this famous type site was clearly required, so that if vegetation characteristic of the Two Creeks Interval were recorded in the Cary kettle, such would be obvious from a comparison of the pollen spectra from Two Creeks with those from the Cary kettle.

As will be seen from the results, expectation was justified, and the effect of the Valders Readvance on the periglacial vegetation was seen in the post-Cary sediments.

¹ Late-glacial and postglacial are locally useful terms. They are used here in the following sense:

Late-glacial. The lower limit is the beginning of the retreat from the Cary Green Lake Moraine; the upper limit is at the retreat from the Valders maximum.

Postglacial. From the end of the late-glacial to the present.

² The nomenclature of the drifts follows Thwaites' classification of the drifts in the area (Thwaites, 1956; Thwaites and Bertrand, 1957).

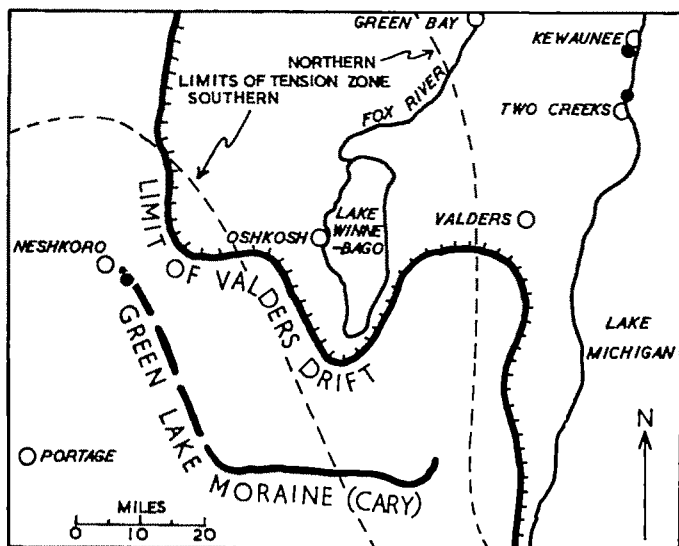


Fig. 1. Map of the area studied. The three sites investigated are shown by the black dots near Neshkoro, Kewaunee, and Two Creeks.

The postglacial vegetational changes in the bog and lake series were also investigated. Considerable differences between them are seen, for they lie on either side of the tension zone (fig. 1). The Cary kettle is in the prairie-forest province and Seidel Lake in the northern hardwoods province (Curtis, 1959).

The pollen samples were treated with KOH and acetolyzed, and with hydrofluoric acid if they contained mineral matter. The pollen diagrams are based on percentages of total pollen excluding the pollen of water plants. The relative proportions of arboreal pollen (AP) and nonarboreal pollen excluding pollen of water plants (NAP) are shown in the pollen diagrams. The sediment symbols used in these diagrams are explained in figure 4. Though no detailed size-statistical work was done, an attempt was made to separate *Picea mariana* pollen from that of *Picea glauca*, and *Pinus banksiana* pollen from that of *Pinus strobus* and *P. resinosa*. After comparison with type slides and with measurements by other authors (Wilson and Webster, 1942; Cain, 1940), size distinctions were drawn as follows:

Picea mariana—total length (grain + wings) less than 100μ

Picea glauca—total length greater than 100μ

Pinus banksiana—grain (i.e. tube cell) length less than 50μ

Pinus strobus-resinosa—grain length greater than 50μ

The pollen grains were not usually in a convenient position for measuring, in which cases the estimation of size was subjective. The consistency of the curves obtained suggests the results have validity. A difficulty encountered was the identification of the pollen grains of *Populus*. Many grains comparable with those of *Populus* were found in the lower zones with *Picea*. But they were not well preserved and because of the uncertainty of identification were not included in the pollen diagrams. By comparison with modern communities with

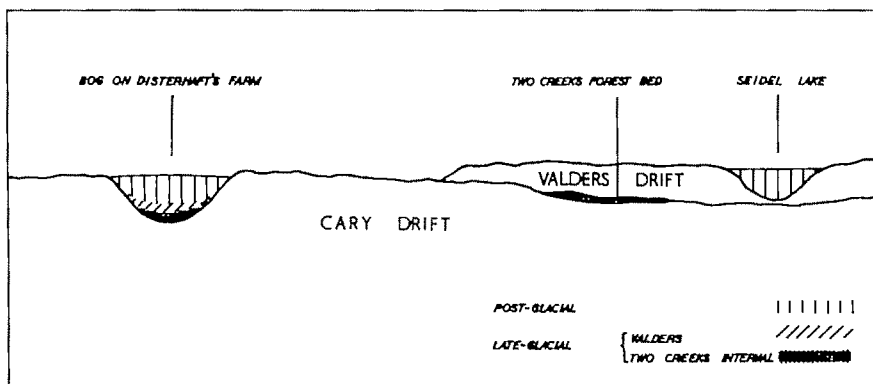


Fig. 2. Sketch of relations between the sites studied and the Cary and Valders Drifts.

Picea of the sort discussed here, *Populus* would certainly be expected. It seems that the preservation of the grains of fossils is not good. However, the doubt about its presence should not very significantly alter the interpretation of the pollen diagrams.

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DESCRIPTIONS OF THE THREE SITES

Two Creeks Forest Bed

The Two Creeks Forest Bed and its position between the Cary and Valders Substages of the Wisconsin Glaciation have been described by Wilson (1932, 1936), Thwaites (1956), and Thwaites and Bertrand (1957). The classical exposures are in the cliffs of the Lake Michigan coast. Here, the two sites studied are located as shown in figure 3. Each site showed the characteristic development of the Forest Bed. A thin layer of organic litter with wood fragments and *Picea* needles occurred over gray silt and clay, being itself overlain by gray-yellow clay, silt, and sand. The Forest Bed at site A was 1 cm thick, at site B 7 cm thick. At neither site was there a well-developed soil beneath the Forest Bed, though at site B the organic matter of the Forest Bed graded into the underlying silt in a way suggesting incipient soil development. Pollen analyses of sediments from sites A and B are given in figure 5. The pollen at site A was not well preserved; that at site B was better preserved but not perfect. At site B pollen was scarce in the upper silt and disappeared above the top analysis. Neither was there any pollen in the silts below the basal analysis.

Disterhaft's Farm Bog

Alden's (1918) account of the Quaternary geology of southeastern Wisconsin describes the Green Lake Moraine as a retreat or perhaps readvance

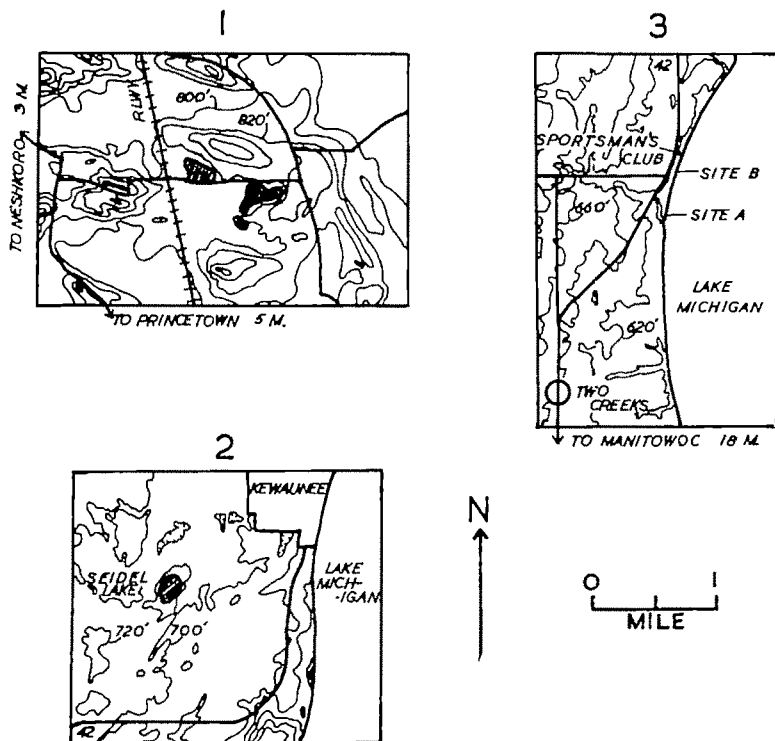


Fig. 3. Locations of the three sites studied: 1. Disterhaft's Farm Bog. The bog is north of the road immediately east of the railway. A dot marks the position of the boring. 2. Seidel Lake. A dot in the southeastern part of the lake marks the position of the boring. 3. Positions of sites A and B, sections showing the Two Creeks Forest Bed.

end moraine of the Green Bay Glacier. The position of this moraine is shown in figure 1. According to the maps of Alden it clearly lies outside the limit of the Red (Valders) Drift, and Thwaites and Bertrand (1957) designate it a Cary moraine. At the northwestern end of this moraine is the town of Neshkoro in Marquette County. About 4 miles southeast of Neshkoro in SE $\frac{1}{4}$ SW $\frac{1}{4}$ section 23, T 17 N, R 11 E lies a bog (altitude above sealevel about 800 ft) in a well-developed hummocky ridge of the Green Lake moraine, here about 10 miles west of the limit of the Valders Drift, as seen in figure 1. The drift around the bog was seen in surface exposure to be a pink stony sand; in this region it overlies Cambrian sandstone. The bog, presumably filling an old kettle, presents a characteristic appearance, with an inner, apparently rather higher community dominated by ericads and *Sphagnum*, and an outer wetter ring of grasses and sedges. The slopes surrounding the bog are covered with patchy woodland, with predominant *Quercus* but also with *Betula*, *Corylus*, *Populus*, *Rhus*, *Salix*, and *Juniperus*.

A boring in the center of the eastern part of the bog was made with a Livingstone sampler. Apart from the difficulty of sampling the matted topmost bog sediments with this type of sampler, a complete series was obtained through the organic sediments filling the hollow. The stratigraphy below 700

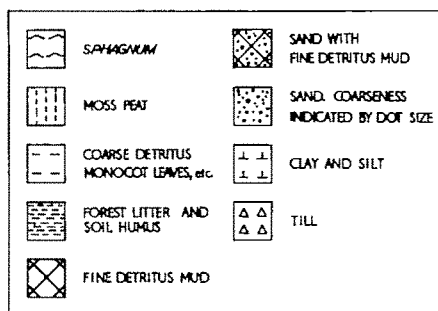


Fig. 4. Sediment symbols used in the pollen diagrams.

cm was checked by a duplicate series of cores. The boring showed the following stratigraphy:

0 to 15 cm	Fresh <i>Sphagnum</i> peat with ericad twigs.
15 to 320 cm	Brown coarse detritus mud with <i>Sphagnum</i> leaves, scattered ericad twigs and leaves, and roots of monocots (40 to 100 cm was lost from the corer).
320 to 710 cm	Brown fine detritus mud, getting increasingly sandy below 670 cm. With <i>Brasenia</i> seeds at about 400 cm.
710 to 830 cm	Gray unsorted sand mixed with fine detritus mud. The sand is coarser (up to 2 mm) from 760 to 790 cm. A pinkish silty clay interrupts the muddy sand from 820 to 826 cm.
830 to 850 cm	White unsorted sand.
850 to 870 cm	Pinkish unsorted sand.

The sediments presumably represent post-Cary time, assuming that dead ice did not fill the kettle for too long. The slow transition to the present bog vegetation is shown in the change in coarseness of the muds towards the top and the concomitant appearance of *Sphagnum* and ericad twigs.

The origin of the sand in the basal unstratified sandy sediments must be considered. The surrounding drift is very sandy. The sand may have been blown into the lake or onto the winter ice by wind. Or it may have been floated in by gentle wave action on the sandy shores, a process requiring little wind, as demonstrated by McKelvey (1941). Or soil creep along the steep east side of the lake may have introduced the sand into the lake. The lack of plant growth in the lake suggested by the small content of organic matter in the sediment would enhance the latter two processes. Whichever of these explanations applies, the presence of the sand indicates nearby sources, itself suggesting open vegetation locally near the lake throughout late-glacial times. The increase in coarseness of the sand at 760 to 790 cm corresponds roughly to the time later correlated with the Valders Readvance (fig. 6). Evidently the deterioration of the climate at this time intensified the processes at work.

Pollen analyses were made from samples through these sediments. Pollen was found at all levels above the white sand, except in the pinkish clay from 820 to 826 cm. The resulting pollen diagram is given in figure 6.

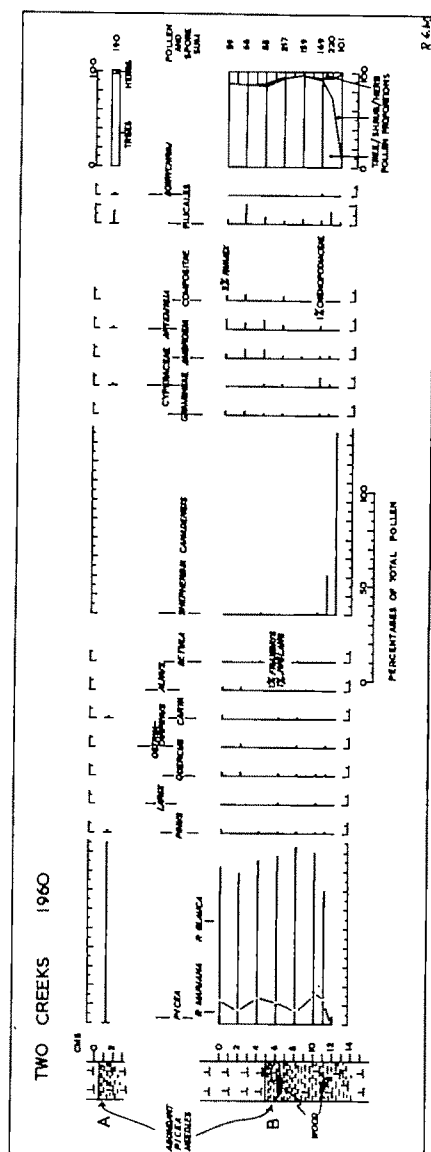


Fig. 5. Pollen diagram from the Two Creeks Forest Bed.

Seidel Lake

Seidel Lake (SE $\frac{1}{4}$ section 24, T 23 N, R 24 E, altitude 691 ft above sea-level) lies in an enclosed hollow 1 mile southwest of the coastal town of Kewaunee (fig. 3). According to the drift map of the Door Peninsula by Thwaites and Bertrand (1957), the hollow is in the ground moraine of the Valders Substage, which itself overlies here a Cary end moraine. The lake is in an area of agricultural land but is surrounded on the slopes of the hollow by woodland. Around the lake is a wide-fringing, partly floating, mat of plants, covered with shrubs (*Alnus*, *Cornus*, *Corylus*, *Vaccinium*) and trees (*Betula*, *Larix*, *Thuja*).

A boring was made with a Livingstone sampler at the edge of the vegetation mat by the southeast corner of the lake. Apart from the difficulties of taking a core through matted sediments with this type of corer, a complete series of cores was obtained down to a basal red stony clay, presumably the Valders Till. The following stratigraphy was observed:

0 to 20 cm	Brown moss peat with roots.
100 to 523 cm	Brown medium-fine detritus mud, coarser and with root-lets towards the top (samples missing from 20 to 100 cm).
523 to 530 cm	Brownish muddy unsorted sand. Sharp boundary at 523 cm, gradual transition below.
530 to 540 cm	Pinkish silty mud.
540 to 600 cm	Brown fine detritus mud.
600 to 635 cm	Pinkish silty or clayey detritus mud.
635 to 700 cm	Laminated red clay and silt and gray sand, with muddy layers at intervals.
700 to 735 cm	Red stony clay (Valders Till).

The series of sediments represent the principally organic infilling of the lake during post-Valders time. The more inorganic layer found at 523 to 540 cm must have been formed during a low water level of the lake, as the contained plant fossils indicate reworking and redeposition of the older basal sediments during its formation. A pollen diagram through the lake sediments is given in figure 7.

3. VEGETATIONAL AND ENVIRONMENTAL HISTORY

Outline Correlation of the Pollen Diagrams

Inspection of the three pollen diagrams, figures 5, 6, and 7, with their stratigraphical relations shown in figure 2 borne in mind, will suggest the following correlations between them:

(a) Correlation between the Two Creeks pollen diagram and the Disterhaft's Farm Bog pollen diagram. High values of *Picea* pollen (80 to 90 percent) prevail in the Two Creeks diagram. Ten to 20 percent of this pollen is of *P. mariana*-type, the rest *P. glauca*-type. Similar *Picea* frequencies with similar proportions of *P. mariana*- and *P. glauca*-types occur in Disterhaft's Farm Bog near the base from 780 to 812 cm. It seems reasonable to suppose that this level in the Bog diagram represents the Two Creeks Interval, with sedimentation starting in the lake basin soon after the retreat of the Cary ice from the Green Lake Moraine.

(b) Correlation between the Disterhaft's Farm Bog diagram and the Seidel Lake pollen diagram. The basal pollen spectra from Seidel Lake must represent the first vegetation to appear in the region on the retreat of the Valders ice. These spectra resemble those from the Disterhaft's Farm Bog phase with lower *Picea* values immediately above the higher *Picea* phase, which has just been correlated with the Two Creeks Interval. Both show the lower *Picea* values and significant percentages of *Quercus*, *Fraxinus*, *Ostrya-Carpinus*, and *Artemisia*. An interpretation of this similarity is that the phase

with lower *Picea* at the Bog represents the periglacial vegetation during the Valders glacial maximum following the Two Creeks Interval. Then when the Valders ice retreated a similar vegetation type migrated northwards, giving the basal spectra seen at Seidel Lake. As this happened, the *Picea* forest again spread in the region of the Bog, giving the higher values seen at the second *Picea* peak. Then in both the Bog and Seidel Lake postglacial vegetational changes ensued as *Picea* was replaced by more thermophilous trees.

Having indicated the main apparent correlations between the diagrams, we may now go on to describe in more detail the vegetational history, starting with the late-glacial.

Late-glacial Vegetational History

The vegetational changes of the late-glacial are seen clearly towards the base of the diagram from Disterhaft's Farm Bog. A threefold zonation has been applied to these changes. The characteristics of the zones will appear in the descriptions of the zones.

Zone 1. The time of retreat from the Green Lake Moraine.—The retreat of the Cary ice from the Green Lake Moraine is reflected in the bottom three spectra of the Bog diagram (812 to 830 cm). These spectra show relatively high NAP values and rising percentages of *Picea* pollen. The *Picea* pollen is mostly *P. glauca*-type. With *Picea* there are small percentages of *Pinus*, *Ulmus*, *Quercus*, *Fraxinus*, *Ostrya-Carpinus*, and *Larix*. Pollen of the shrubs *Elaeagnus commutata* and *Shepherdia canadensis* was also recorded from the zone. The principal herb pollen types are Gramineae, Cyperaceae, *Ambrosia*, and *Artemisia*. The vegetation suggested by these spectra is *Picea*-dominated, with a fair degree of opening amongst the trees. A similar vegetation type is present in zone 3 and further discussion of it will be delayed until the description of zone 3.

Zone 2. The Two Creeks Interval.—At Disterhaft's Farm Bog, the values of *Picea* pollen, which started rising in the time of zone 1, reach a maximum (88 percent of the total pollen) during the time correlated with the Two Creeks Interval (780 to 812 cm). Correspondingly the NAP total falls to a minimum in this zone. Also at low values compared with zones 1 and 3 are *Ulmus*, *Quercus*, *Fraxinus* and *Ostrya-Carpinus*, and also *Picea mariana*-type. The changes from zone 1 to 2 reflect the closing of the *Picea* forest, apparently dominated by *P. glauca* but with some *P. mariana*. A similar forest type is suggested by the analyses (fig. 5) from the Two Creeks site, 84 miles to the east, and also by Potzger's analyses (Zumberge and Potzger, 1956) of organic sediments correlated with the Two Creeks Interval on the east coast of Lake Michigan at South Haven.

At Two Creeks, Wilson's studies (1932, 1936) of the palaeoecology of the Forest Bed showed three stages of environmental history. An early phase with aquatic and semiaquatic molluscs, a middle phase with moist to dry woodland mosses, and a final phase of flooding, with aquatic molluscs and mosses.

The fluctuations of water level result from the changes in drainage of Lake Michigan. When the Cary ice retreated the northern low outlet of the lake (Straits of Mackinac) was exposed, and the water level fell (Bowmanville Stage), allowing the deposition of the terrestrial Forest Bed. The level rose

again as the advance of the Valdres ice closed the Straits, and the site of the Forest Bed was then flooded (Calumet Stage).

The pollen spectra in figure 5 give additional details of the vegetational changes associated with these changes in water level. The abundance of *Shepherdia canadensis* pollen at the base of the sediments indicates early colonization by this shrub of the land surface exposed by the lowering of the lake level. *Shepherdia canadensis* is a northern and montane plant, found in forest clearings and on sandy shores, particularly in the boreal forests with spruce. Thus the plant's behavior at the beginning of the Two Creeks Interval exactly parallels its present behavior. The phase with *Shepherdia* was short-lived and *Picea* forest succeeded the pioneer community, as indicated by the high frequencies of *Picea* pollen. As at Disterhaft's Farm Bog, *P. glauca*-type pollen is far more abundant than *P. mariana*-type. Wilson reported finds of *P. mariana* cones only, but he also recorded the probability that some of the wood was *P. glauca*. The maximum number of annual rings found by Wilson in one log was 142, giving a minimum time for the length of formation of the Forest Bed. The tree rings were generally found to be decreasing in width near the bark, possibly a sign of the rise in water level following the Valdres Readvance. The flooding of the forest litter by the upper silts is accompanied by a large decrease in pollen frequency. At the same time the NAP total, including *Ambrosia*, *Artemisia*, Compositae, rises slightly. This may perhaps reflect the opening out of the regional forest associated with the Valdres Readvance. But then there is also the possibility that some or all of the pollen in the silts is secondarily derived.

The vegetation of the Two Creeks Interval is clearly boreal in character. Originally Wilson (1932) compared the climate to that of northern Minnesota or somewhat colder. In his later paper (1936) he suggested that the climate was not necessarily as severe as this, for "though the fossil plants have a decided boreal character they also represent the pioneer organisms of denuded areas under certain conditions and are therefore not reliable indicators of a severe climate." This question is further discussed in a later section.

Zone 3. The Valdres Readvance.— In the time of this zone (725 to 780 cm) at Disterhaft's Farm Bog, the *Picea* pollen frequencies fall to lower values; *Ulmus*, *Quercus*, *Fraxinus*, *Ostrya-Carpinus*, and *Picea mariana* frequencies rise, and so does the NAP total, mostly because of the increased frequency of *Artemisia*, though the Gramineae and Cyperaceae also rise slightly. The lower position of the boundary can be conveniently placed at the rise of *Picea mariana*-type pollen, the upper limit at the recovery of the *Picea* curve. Evidently the closed forest of the Two Creeks Interval opened out, allowing an increase in the NAP representation. The forest deterioration can be related to the approach of the Valdres ice, which at its maximum reached a limit about 10 miles east of the site. The rise in *Picea mariana*-type pollen may result from the increased wetness of low-lying terrain as the Valdres ice approached. A similar rise in *P. mariana*-type pollen during a time correlated with the Valdres Readvance is seen in Potzger's pollen diagram (Zumberge and Potzger, 1956) from South Haven, on the east coast of Lake Michigan. Ritchie (1957) noted in northern Manitoba the replacement of *P. glauca* by *P. mari-*

ana in areas where wetness favored peat accumulation. Today *P. mariana* is a characteristic tree of the northern swamp forests of Wisconsin, though farther north the tree is also characteristic of upland sites.

A problem arises in the interpretation of this part of the pollen diagram: what is the significance of the increase in the pollen frequencies of the deciduous trees (*Ulmus*, *Quercus*, *Fraxinus*, *Ostrya-Carpinus*) seen in zone 3, and also zone 1? An answer to this question is not easy to provide. Three explanations are possible: a. That the trees grew sparsely in the spruce woodland, either scattered generally or in locally specialized habitats. b. That the opening of the spruce forest in zones 1 and 3 allowed pollen from distant sources to be blown into the area. c. That they are secondarily derived by reworking of older deposits.

This third possibility was suggested by Andersen (1954) to explain the presence of trees such as *Ulmus*, *Quercus*, *Fraxinus*, *Ostrya-Carpinus* in late-glacial clays with *Picea* pollen in Michigan. To prove such a contention it is necessary to find older sediments from which the pollen might have been derived. Analyses of the sand below the fossiliferous muddy sand showed no pollen present. Neither was pollen found in analyses of Valders till below the Seidel Lake sediments, although *Ulmus*, *Quercus*, *Fraxinus*, and *Ostrya-Carpinus* are present with dominant *Picea* in the lowermost inorganic lake sediments. There seems to be no reason to suggest that these pollen types are derived from older deposits by reworking.

This leaves the first and second possibilities mentioned above. At Seidel Lake *Ulmus*, *Quercus*, and *Ostrya-Carpinus* frequencies rise towards the end of the *Picea*-dominant zone. This suggests that these trees were available to colonize the soils exposed by the Valders retreat at no great distance from the limit of the Valders maximum. On the other hand, at Disterhaft's Farm Bog the rise of the deciduous tree pollen types accompanies the opening out of the forest indicated by the NAP rise. Such an effect could result from the increased likelihood of the deposition of distantly derived pollen in areas with open vegetation, compared with conditions in a closed forest of the Two Creeks type. A third point is that whereas *Picea* and the NAP curve behave in a way consistent with a climatic fluctuation related to a glacial readvance, the deciduous tree curves do not, as they rise at the time of the climatic deterioration. This suggests that the climatic deterioration mainly affected the local spruce forest. These considerations suggest the following explanation of the presence of these deciduous trees in zones 1 and 3: that they were present in the region in one or more of the diversified habitats to be expected, probably quite distant, not necessarily in the open spruce woodland.⁵ For example, it might be suggested that species of *Ulmus*, *Quercus*, *Fraxinus*, and *Ostrya-Carpinus* might have been growing in moist riverine habitats. These genera (except *Ostrya*) have species characteristic of such habitats, and their distribution overlaps with *Picea* at the present day. In addition, *Ulmus*, *Quercus*, and *Fraxinus* have species reaching into the boreal forest (*U. americana*, *Q. macrocarpa*, *F. nigra*). If this explanation is correct then obviously the

⁵ Woodland is used here in the sense described by Hare (1950), to suggest spacing of the trees.

presence of these genera has a climatic significance, which will be discussed later.

Evidence for such vegetational conditions would be provided by modern pollen spectra showing a similar composition. Such analyses are insufficient to make any good comparisons, but a sample from moss polsters in spruce-oak "parkland" north of the Spruce Woods Forest Reserve in southern Manitoba does help to illustrate the kind of vegetation present. The analysis is shown in table 1; it is calculated on the same basis as the fossil analyses. Unfortunately no time was available to survey the vegetation around the polsters. An account of the vegetation in the region has been given by Bird (1927, 1930). It is more a stunted woodland with openings than an open parkland. The soil is sandy. The commonest trees are *Picea*, *Quercus*, *Betula*, and *Populus*. No *Abies* was seen. The vegetation is really an open variation of the southeastern type of the mixed wood section of boreal forest, judging by Rowe's (1959) classification of the forest regions of Canada. The pollen analysis shows 32 percent NAP, mostly *Ambrosia*, *Artemisia*, and *Chenopodiaceae*. Clearly there is some resemblance to the vegetation already described from the late-glacial zones 1 and 3.

We may summarize our account of the vegetation by saying that in the time of zone 3 (and 1) spruce-dominated fairly open woodland existed in the region outside the Valdres ice in the region of the Green Lake Moraine. Deciduous trees were present, probably distantly, in locally favorable habitats, perhaps in riverine situations. Amongst the herbs in the openings in the woodland grew *Artemisia* and other composites, grasses and sedges.

Late-glacial Climate

First, the question of the general climate of the late-glacial must be discussed. Here the interpretation of the *Picea* frequencies plays a dominant part. Wilson (1938) demonstrated that *Picea* behaved as a pioneer on the successively younger series of soils in northern Wisconsin. The evidence suggests that *Picea* is not necessarily an indicator of boreal climate but rather the tree best able to colonize the soils left bare, in this case, by the successive lowerings of the level of the Great Lakes in late- and postglacial time. (Similarly, *Picea* pollen has been found in high frequencies at the base of lake sediments as far south as Indiana (Potzger, 1946)). On the other hand, Leopold (1958) has suggested from a study of the late-glacial behavior of spruce in New England and its present distribution in relation to the July isotherms that the July temperature of the Two Creeks Interval was 3-5°C lower than that of the present day (21°C), and that of the Valdres Readvance 4-5°C lower.

A good indication of climate would come from the presence of warmth-demanding species. Here we are at a disadvantage because of the paucity of specific identifications of pollen and macroscopic plant remains. In the pollen diagrams given here the presence of the deciduous trees indicates a climate more favorable than that, say, of northern or north-central Manitoba. As regards the warmth maximum it cannot be said that spruce forest or woodland definitely indicates a certain upper limit of temperature, as at present the southern limit of spruce, running near the 21°C July isotherm, is determined

the Earth's surface on landing, presumably because it fell at reduced speed with its thickest wall forward on soft soil. It subsequently survived, without any major visible effects, the activities of subaerial agents of erosion. Other, usually smaller, examples of hollow australites have been found, but these are either (a) in a broken condition (Baker, 1956, pl. II, fig. 11; 1957, pl. I, fig. 3), (b) affected by solution-etching (Baker, 1956, pl. II, figs. 9 and 10), or else (c) they reveal the internal cavity has been penetrated and exposed by ablation of part of the front wall during flight and the lip of the opening rounded by melting.

The only known complete hollow australite (not sliced) is from Kangaroo Island off the coast of South Australia (Stelzner, 1893; Suess, 1900), and this differs fundamentally from the hollow form redescribed herein being smaller and in revealing that some melt glass appears to have been frozen-in around its equatorial periphery. As a result, the depth of ablation is proportionally smaller in the Kangaroo Island specimen, and the total glass lost by ablation and melting is considerably less.

No adequate explanation has yet been advanced for the mode of origin of the parent forms of hollow tektites at their extraterrestrial birthplace.

SUMMARY OF MEASUREMENTS AND CALCULATIONS FOR THE
HOLLOW AUSTRALITE FROM UPPER REGIONS STATION, NEAR HORSHAM,
WESTERN VICTORIA

(1) Diameter of form (measured along the rim)	59.0 mm
(2) Depth (normal to the rim; measured along the polar axis) = (4) + (10) + (11)	53.5 mm
(3) Width of internal cavity	44.5 mm
(4) Depth of internal cavity	47.0 mm
(5) Radius of curvature (R_B) of posterior surface (external)	30.5 mm
(6) Radius of curvature (R_F) of anterior surface (external)	27.5 mm
(7) Radius of curvature of back surface of internal cavity	22.0 mm
(8) Radius of curvature of front surface of internal cavity	22.0 mm
(9) Diameter of original hollow sphere ($D_i = 2R_B$)	61.0 mm
(10) Thickness of rear walls (common to hollow australite and original hollow sphere)	2.5 mm
(11) Thickness of front walls of hollow australite (reduced by ablation)	4.0 mm
(12) Thickness of front walls of original hollow sphere	11.5 mm
(13) Depth of ablation (= (12) - (11)) at the stagnation point	7.5 mm
(14) Thickness of equatorial walls (at the rim)	7.5 mm
(15) Sum of weights of tektite glass in the two sliced portions ..	90.797 gm
(16) Calculated weight of tektite glass lost by slicing (average of results obtained by two different methods)	3.358
(17) Weight of glass original to the complete hollow australite ..	94.155 gm
(18) Weight of tektite glass in primary hollow sphere	167.00 gm
(19) Weight of tektite glass ablated (= (18) - (17))	72.86 gm

the same specific gravity as the remaining glass constituting the two separate sliced portions.

The specific gravity of the complete specimen, determined in 1898, is recorded in the catalogue of specimens in the collection of the National Museum of Victoria as 1.06, but the weight of the specimen as a complete entity is not given. As a check on the weight of glass lost by slicing, the mass of the complete specimen was first determined from:

$$M = \frac{D_G \times D_{HS} \times V_{IO}}{D_G - D_{HS}},$$

where D_G = specific gravity determined for the glass of the sliced portions, D_{HS} = specific gravity of the complete hollow specimen, and V_{IO} = calculated volume of the internal cavity. This gave a value of $W = 94.048$ gm as the weight of the complete hollow australite, and as the weight (w_1) of the glass constituting the two sliced portions is 90.797 gm, the weight of glass lost (w_2) during the slicing process is therefore $W - w_1 = w_2 = 3.251$ gm. This is 0.214 gm less than the amount lost as determined by the first method (above). The average (3.358 gm) of the two results has been used in subsequent calculations, and on this basis, the total weight of the hollow australite after it had been ablated by aerodynamic heating is 94.155 gm.

AMOUNT ABLATED

The amount of glass removed from the parent form by ablation through aerodynamic heating can be determined approximately from the difference between the calculated volume of glass originally present in the primary hollow form and that measured in the hollow australite.

The volume of the original hollow sphere with a radius of curvature of 3.05 cm is calculated as 118.84 cm³. The volume of the glass in the residual hollow australite determined from the mass and specific gravity is 38.86 cm³. This leaves 79.98 cm³ for the volume of the internal cavity plus the volume of the glass lost by ablation.

The volume of the internal cavity, calculated as the sum of the volumes of caps of spheres with similar heights (2.35 cm) and similar radius of curvature (2.2 cm) is 49.91 cm³. Hence the volume of glass ablated is approximately 30.07 cm³.

The mass of this volume of glass lost by ablation, assuming its specific gravity to have been the same as that of the residual glass, is 72.86 gm. The total weight of glass in the original hollow sphere was thus approximately 167 gm. The amount removed represents a 25 percent loss of volume purely by the ablation of tektite glass on transition from the primary hollow sphere to the secondary hollow australite shape, and this involved a 43.6 percent removal of glass by the ablation process.

The internal cavity was not penetrated and exposed by the final level to which ablation progressed, and hence remained intact throughout (i) the period of initial entry into the atmosphere, (ii) the ablative phase, and (iii) the end phases of flight and ultimate landing upon the Earth's surface. The preservation of such a hollow form in the complete state as found, is remarkable and of extremely rare occurrence. It withstood the force of impact with

of arcs of curvature yields a slightly elliptical outline, but the small re-entrants where they meet in the graphical constructions are not evident in this hollow australite, although one specimen is known (see Baker, 1959, pl. XIV, no. 2) where the re-entrants are large, resulting in a dividing septum and an apparent double internal cavity.

Since the posterior surface is evidently a nonmodified remnant of the original sphere, and still reveals about 45 percent of the arc of curvature of a sphere, the radius of curvature of its external wall gives the original diameter of the parent form ($2R_B = 61$ mm) and is necessary to calculation of the volume and mass of the original sphere.

The radius of curvature of the anterior surface (external wall) is numerically slightly lower because of ablation of the forwardly directed part of the original sphere surface. It was regularly ablated in such a way as to produce a smaller, virtually hemispherical surface that was not quite as smooth as the primary surface, but which developed a steeper arc of curvature.

WEIGHT, SPECIFIC GRAVITY, AND VOLUME

The two portions of the sliced hollow australite weigh 46.565 gm and 44.232 gm respectively. The specific gravity of each is 2.423 as determined in distilled water ($T = 14.5^\circ\text{C}$) on a chemical balance; this is higher than usual for the glass constituting hollow australites, most fragments of which have specific gravity values under 2.400.

The sum of the two weights (90.797 gm) is not the total weight of the complete hollow australite, as allowance has to be made for glass lost by cutting during the slicing process. The thickness of the cut has been estimated from reconstruction to be approximately 2 mm and the volume and mass lost during slicing as 1.43 cm^3 and 3.465 gm respectively.

The volume of the glass lost (V_L) by slicing the specimen was calculated from:

$$V_L = V_O - (V_{IO} + V_{GW} + V_A), \text{ where}$$

V_O = volume of original hollow form calculated from $4/3 \pi (R_B)^3$.

V_{IO} = volume of internal cavity obtained from the sum of the volumes of the caps of spheres of measured radius of curvature and measured height from the radical line (KL' in fig. 1) to the pole position (N and M in fig. 1), i.e. $V_{IO} = \pi/3 (h_1^2(3R_B - h_1) + (h_2^2(3R_F - h_2)))$, where $h_1 = AR$ and $h_2 = BR$ in figure 1.

V_{GW} = volume of glass weighed (two halves with the same specific gravity)

V_A = volume ablated, as obtained by difference ($V_O - V_{HA}$), where V_{HA} = volume of hollow australite obtained from the sum of the volumes of the caps of spheres of measured radius of curvature and measured height from rim (XY in fig. 1) to pole positions (N and M in fig. 1), i.e. $V_{HA} = \pi/3 (d_1^2(3R_B - d_1) + d_2^2(3R_F - d_2))$, where d_1 = height of posterior cap (=NQ in fig. 1), d_2 = height of anterior cap (=QM in fig. 1), R_B = radius of curvature of posterior surface, and R_F = radius of curvature of anterior surface.

The mass of glass lost (3.465 gm) by slicing was obtained from $M = DV$, assuming that the calculated volume of glass lost during slicing possessed

intersecting coaxial circles with collinear centers circumscribed about the posterior and anterior surfaces respectively; NQ = depth of posterior cap; QM = depth of anterior cap; F.S. = flow swirls on posterior surface; I.R. = irregular ridges on anterior surface.

In the hollow australite sketched in figure 1, the depth of ablation (MP) is approximately the same as the distance (OQ) that the rim has migrated rearwards from the original position of the equator of the sphere as aligned in aerodynamically stable orientation. This indicates that, at the level of ablation represented by the ultimate anterior surface boundary, depth of ablation in the stagnation point regions was little different from that occurring radially outwards towards the equatorial regions. The elliptical internal cavity is eccentrically disposed nearer to the back than the front pole of the specimen as depicted in a stable position of flight (fig. 1). A feature of note is that ablation of the anterior surface in the rim region has transected some of the original flow swirls on the primary sphere surface (fig. 1B).

DIMENSIONS

The hollow australite was originally a hollow sphere 61 mm in diameter, but ablation of the front surface has yielded a secondarily shaped form 59 mm across its largest diameter (i.e. as measured along the rim), and 53.5 mm along its shorter diameter (i.e. this is equivalent to the depth of the form, the orientation of the specimen being with its polar axis (NM) in the flight direction).

The internal cavity is 44.5 mm wide and 47.0 mm in depth, and thus slightly elliptical in longitudinal section. The diameter in the third dimension has been found by reconstruction of the sliced form to be also 44.5 mm, so that the complete cavity resembled the shape of a biaxial ellipsoid with the longer axis slightly greater than the equal lateral axes.

During atmospheric flight the hollow specimen was orientated with the longer axis of the internal cavity aligned in the projected flight direction (fig. 1) and with the thickest wall forward. This position of aerodynamically stable orientation was initially predetermined prior to, and evidently maintained by, the hollow form during the ablative phase of its atmospheric flight earthwards. The walls of the hollow form are 2.5 mm thick at the rear pole and 4 mm thick at the front pole (i.e. at the stagnation point). Around the equatorial regions, the glass is thickest in the vicinity of the rim, measuring 7.5 mm on each side of each half of the sliced specimen.

RADII OF CURVATURE

The previously determined radii of curvature (Baker, 1959) of the external and internal walls of the posterior (R_B) and anterior (R_F) surfaces respectively have been rechecked by more refined techniques and found to be: R_B (external) = 30.5 mm; R_B (internal) = 22 mm; R_F (external) = 27.5 mm, and R_F (internal) = 22 mm.

The R_B and R_F values for the internal walls are numerically the same, and the centers of these two coaxial curvatures are collinear but not coincidental. The centers lie on the polar axis, equally spaced on either side of the radical line (K'L' in fig. 1) and approximately 3 mm apart. This combination

The smoother, larger surface (posterior surface) reveals the sculpture pattern described by Walcott to be dominated by a number of flow swirls (fig. 1B) ranging up to approximately 40 mm across, with numerous superficial bubble impressions in between. These are regarded as primary sculpture features developed in an extraterrestrial environment. The sculpture of the anterior surface (fig. 1B) is secondary in origin and due to the effects of aerodynamic friction. Neither surface has been significantly affected by the tertiary processes of subaerial weathering during the few thousand years that the specimen has lain upon or within a layer of topsoil on the Earth's surface.

The two differently sculptured surfaces of unequal size are separated by a sharply defined rim (fig. 1B), which is the peripheral ridge of Walcott's terminology. There is no evidence that a circumferential flange was ever developed on this specimen. The anterior surface reveals a weakly developed flaked equatorial zone on the anterior side of the rim (fig. 1). Comparable features are encountered on the australite cores that are solid throughout, and on them no evidence has yet been noted of flanges tending to develop when a flaked equatorial zone is present; it is usual for such specimens to reveal a sharply marked rim delineating the anterior and posterior surfaces.

The walls of the internal cavity show a high degree of "hot polish", having a highly vitreous luster, freedom from schlieren, and hence a mirror-like reflecting surface. When held up to a strong light, the translucency of each sliced portion of the hollow australite is readily observed, more particularly where thinner in the vicinity of the rear pole on the posterior cap of the specimen.

The different characteristics of the sculpture patterns of the posterior and anterior surfaces are sketched in figure 1, which also shows the terminology used for the hollow australites.

In figure 1, *for the parent hollow sphere*, O = mid-point; N = back pole; P = front pole of the form as aligned in aerodynamically stable orientation and also represents the initial stagnation point. EF = diameter = equatorial axis of the specimen when oriented in the line of flight; NP = polar axis, lying in the projected flight direction, but is not an axis of rotation; OE = radius of curvature of the posterior surface.

For the internal cavity, AB = depth; K'L' = width (AB is greater than K'L'); K'AL' = rear half of elliptical cavity; K'BL' = front half of elliptical cavity; R = mid-point; AR = depth of posterior cap; RB = depth of anterior cap.

For the ablated form (= hollow australite), XY = width, and this marks the position of the circumferential rim that delineates the posterior (XNY) from the anterior (XMY) surface; NM = depth = the polar axis of the specimen as aligned in stable aerodynamic orientation, under which condition it is not an axis of rotation; N = back pole; M = front pole and represents the position of the stagnation point during the final stages of ablation; NA = thickness of back wall; BM = thickness of front wall; XC = DY = thickness of walls as measured from cavity to rim; MP = depth of ablation at the stagnation point; OE = radius of curvature of posterior surface; RM = radius of curvature of anterior surface; KL = radical line = chord common to the

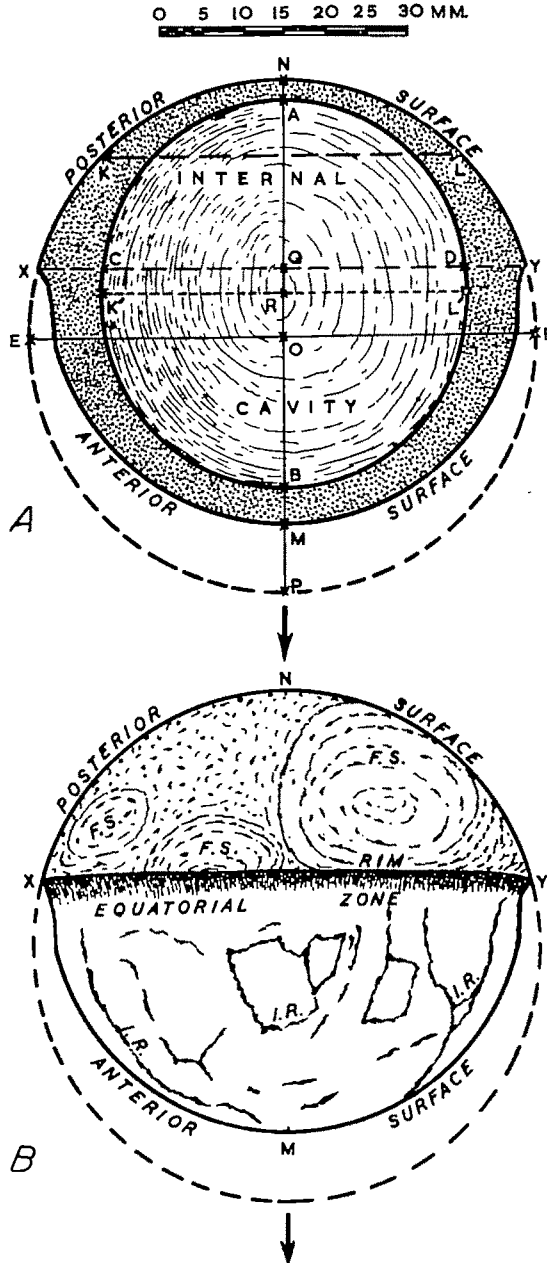


Fig. 1. Sketch diagram of sliced hollow australite from Upper Regions Station, near Horsham, western Victoria.

A—showing inside aspect of one of the sliced portions with eccentrically disposed elliptical internal cavity having smooth walls; the inside aspect of the other portion is identical in appearance with that depicted.

B—external surface showing flow-swirled and bubble-pitted sculpture of posterior surface, irregular flow ridges, and equatorial zone on the anterior surface. This is the same half that Walcott (1898) figured; the other portion of the specimen reveals a slightly different distribution of the sculpture elements, the posterior surface possessing a large flow swirl 40 mm across.

The arrow indicates direction of downward flight through the Earth's atmosphere. In figure 1A, the stippled areas represent australite glass; the thin curved broken

cut. It has been possible to form a relatively accurate assessment of the amount of glass removed by slicing.

The same specimen was later figured by Dunn in two different publications. One of these (1908, pl. XXXIII, no. 4 and pl. XXXIV, no. 4) does not give the locality from which the specimen was collected. The other (1912, pl. 7, nos. 2 and 2A) lists the specimen as coming from Hamilton, Victoria, which is just over 60 miles west of south of Horsham. Dunn's illustrations in his two separate publications are prints from the same negative but are different from Walcott's original photographs, as indicated by the different types of reflections from the highly vitreous walls of the internal cavity. Since neither set of illustrations is quite to natural scale, Walcott's being slightly oversize and Dunn's undersize, they cannot be utilized in obtaining accurate measurements of the specimen. Comparison of the details of the sculpture patterns in both Walcott's and Dunn's illustrations reveal that the specimen described is one and the same. Only one such specimen is known in tektite collections in Melbourne, and as it is catalogued in the register book of the National Museum of Victoria as being from Upper Regions Station, Horsham, western Victoria, this is taken to be the correct locality.

DESCRIPTION OF SPECIMEN

Walcott (1898, p. 33-34) described the Horsham hollow australite as approximately spherical with "its greatest diameter across the peripheral ridge" measuring "59 mm., and at right angles to this, 52.5 mm." Its characteristic form was described as being that of "two hemispheres of unequal diameter joined together". The interior "which is slightly egg-shaped, has its greatest diameter of 47.5 mm. in the direction of the smallest outside diameter. The other inside diameter measures 44.5 mm." The interior of the form is "perfectly smooth and has a high polish". Walcott also noted that the walls of the hollow australite as observed after slicing were "quite dense, with the exception of a few scattered vesicles" and consisted of glass which was "a brownish colour in transmitted light". He described the outer portions of the larger of the two hemispherical surfaces as "generally smooth and marked with pittings crowded into irregular bands or patches enclosing smooth elliptical centres", and the smaller as showing "peculiar corrugations commencing immediately under the peripheral ridge, but gradually fading away as the centre . . . is approached". It also shows pits but "to a much lesser extent and more equally distributed", and "marks or short grooves, in their arrangement somewhat resembling Hebrew characters, commencing at a slightly raised centre and radiating in six irregular lines towards the (peripheral) ridge".

The larger curved surface is the posterior surface of recent terminology; it represents that part of the original surface of the parent extraterrestrial form that remained directed away from the Earth during atmospheric flight, and does not seem to have been secondarily affected in any way by aerodynamic heating. The smaller curved surface is the anterior surface; because it was projected in the line of flight during atmospheric transit at high speeds, it has consequently been modified by ablation arising from heating by aerodynamic friction during direct single-pass entry at ultrasupersonic velocity.

A PERFECTLY DEVELOPED HOLLOW AUSTRALITE*

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ABSTRACT. A rare hollow australite found as a complete, non-weathered specimen near Horsham, western Victoria towards the close of the last century, was cut into two nearly equal portions to reveal the nature of the internal cavity, and the sliced specimen was described by R. H. Walcott in 1898.

It has been re-examined in the light of recent research work on re-entry phenomena and shown to have resulted from the ablation of a primary sphere of tektite glass containing a relatively large, eccentrically disposed elliptical internal cavity. During high speed unidirectional fall to Earth through the Earth's atmosphere, the specimen maintained aerodynamically stable orientation, so that only the thicker forwardly directed surface of the glass shell was subjected to ablation resultant upon aerodynamic frictional heating. This process resulted in a loss of 43.6 percent of tektite glass from the original hollow sphere without penetrating the internal cavity.

INTRODUCTION

A perfectly developed and exceptionally well-preserved hollow australite found at Upper Regions Station, near Horsham in western Victoria, was presented to the National Museum of Victoria (Reg. No. 5204) by Mr. Thomas Edols towards the close of the nineteenth century. It was sliced along the plane containing the polar axis into two almost equal portions, after its specific gravity was found to be very low (1.06) for australites generally. The specimen was originally described and figured by Walcott (1898, p. 33-34 and pl. III, figs. 1, 1a).

Through the courtesy of the Director, Mr. C. W. Brazenor, the author has been enabled to examine the form and sculpture patterns of the two halves of this very rare specimen, and facilities were provided by the Curator of Minerals, Dr. A. W. Beasley, for the determination of the weights and specific gravity of the two portions. Two plaster casts of each half were also available for examination.

The specimen assumes importance in view of recent re-entry research to the cosmic origin of tektites (Chapman, 1960) and to overseas research work connected with the development of manned spacecraft and heat shields. For these reasons, it is pertinent to add further details to Walcott's (1898) original description, and to utilize recently published data on surface curvature measurements (Baker, 1959) in the determination of the mass and volume respectively of the reconstructed complete hollow australite and of the hollow parent form from which it was developed. From the data so obtained can be calculated the amount of tektite glass ablated from the primary form by aerodynamic heating generated by friction of the atmosphere against its forwardly directed surface during ultrasupersonic infall to the Earth's surface.

Because the internal cavities are under negative pressure, hollow tektites frequently implode and shatter to many pieces when attempts are made to slice them, but the Horsham specimen successfully withstood the slicing operation so that the only glass lost in this way is accounted for by the thickness of the cut and a few small chips lost by fracture from the edge of the plane of the

* Contributions of the Meteoritical Society, vol. 6, no. 8.

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It is known that throughout most of Pennsylvania the Devonian red beds that are lithologically related to those of the Catskill type area in New York are limited to the Upper Devonian sequence (Willard, 1939, figs. 72 and 74). In the Delaware Valley of eastern Pennsylvania, where the oldest Devonian red beds occur, the basal Catskill (Analomink) is approximately middle "Portage" (Upper Devonian) or slightly younger (Willard, 1939, p. 263).

In eastern New York, on the eastern side of the Schoharie Valley, the oldest red beds of the nonmarine Catskill facies appear a little above the middle of the Middle Devonian Hamilton Group, but farther east in Albany and Greene counties most of the Hamilton Group above the Marcellus Formation consists of nonmarine beds (Cooper, 1933, p. 539).

In north-central New Jersey the very coarse-grained, red Skunnemunk Conglomerate began to form in late "Marcellus time" and continued into the Upper (Late) Devonian (Willard, 1939, p. 262).

Thus, the lower limit of the Catskill Formation changes quite drastically from west to east, from younger to older rocks. In eastern New York and north-central New Jersey, therefore, where the red beds of the Catskill Formation replace a major portion of the Hamilton Group, the base of the Susquehanna Group should be defined as the base of the red beds rather than the top of the Hamilton Group, since one of the practical aspects of the Susquehanna Group is to embrace all red beds of the Devonian red magnafacies. The proposed nomenclatural framework set forth in this paper, however, is primarily for use in Pennsylvania and as such restricts the Susquehanna Group to those rocks below the Pocono Formation and above the Hamilton Group.

One other important factor to consider is whether the Upper Devonian red beds of the Delaware Valley in northeastern Pennsylvania are laterally continuous with the Middle Devonian red beds of eastern New York (fig. 3a) or whether the red beds of Pennsylvania are related to but not continuous with the red beds of eastern New York (fig. 3b). Most workers in the area express the opinion that the red beds of the Catskill Formation in Pennsylvania can be traced laterally into the Middle Devonian red beds of the Catskill region of New York (fig. 3a). Thus there is apparently a continuous red bed facies, and it seems justifiable to use the term Catskill Formation for the upper, red non-marine unit. However, if the Upper Devonian red beds of Pennsylvania cannot be traced laterally into the Middle Devonian red beds of the Catskill Mountains, then the term Catskill should be abandoned in Pennsylvania and should be replaced by the term Hampshire Formation, as used by Darton (1892, p. 13, 17, 18) and Butts (1945, p. 13), or some similar rock term indicating Upper Devonian red beds of Catskill type.

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shows the transitional Pocono-Catskill contact. Section #2, on the east side of the Juniata River at Newport, exposes a nearly complete section of the Catskill and transition formations. Section #3, on the west side of the Susquehanna River opposite Clempson Island, is an excellent exposure which includes the Upper Devonian marine beds and most of the transition formation. A complete section of the proposed Susquehanna Group can be compiled from these three exposures. Additional detail can be compiled from section #4, which is an exposure of the Pocono-Catskill contact on the east side of the Susquehanna River at Clarks Ferry. Other partial sections in the area provide additional information which will define the initial subdivisions of the Susquehanna Group.

DISCUSSION

The top of the Catskill red beds throughout Pennsylvania is not everywhere synchronous with the Devonian-Mississippian break (Willard, 1939, p. 282-283). Although this is realized, it is still justifiable when defining the lithologic units to place the top of the Susquehanna Group at the top of the red beds. Detailed mapping will point up variations in the Pocono-Catskill red bed contact, so that the upper limit of the Catskill Formation must be arbitrarily controlled on a local basis by the geologist in the field.

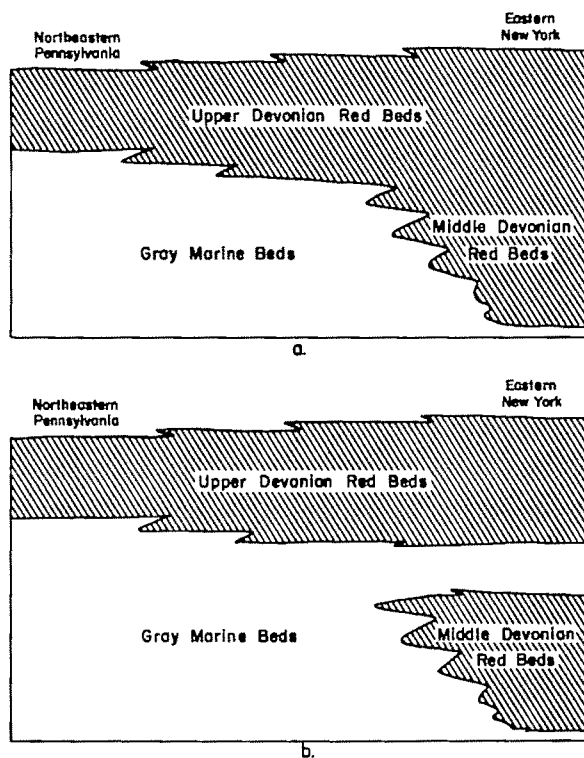
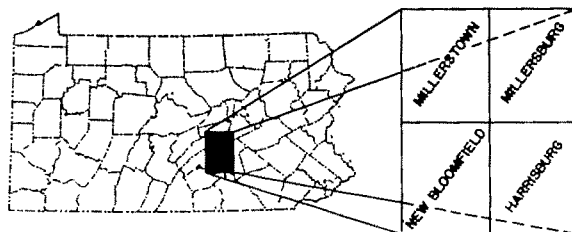
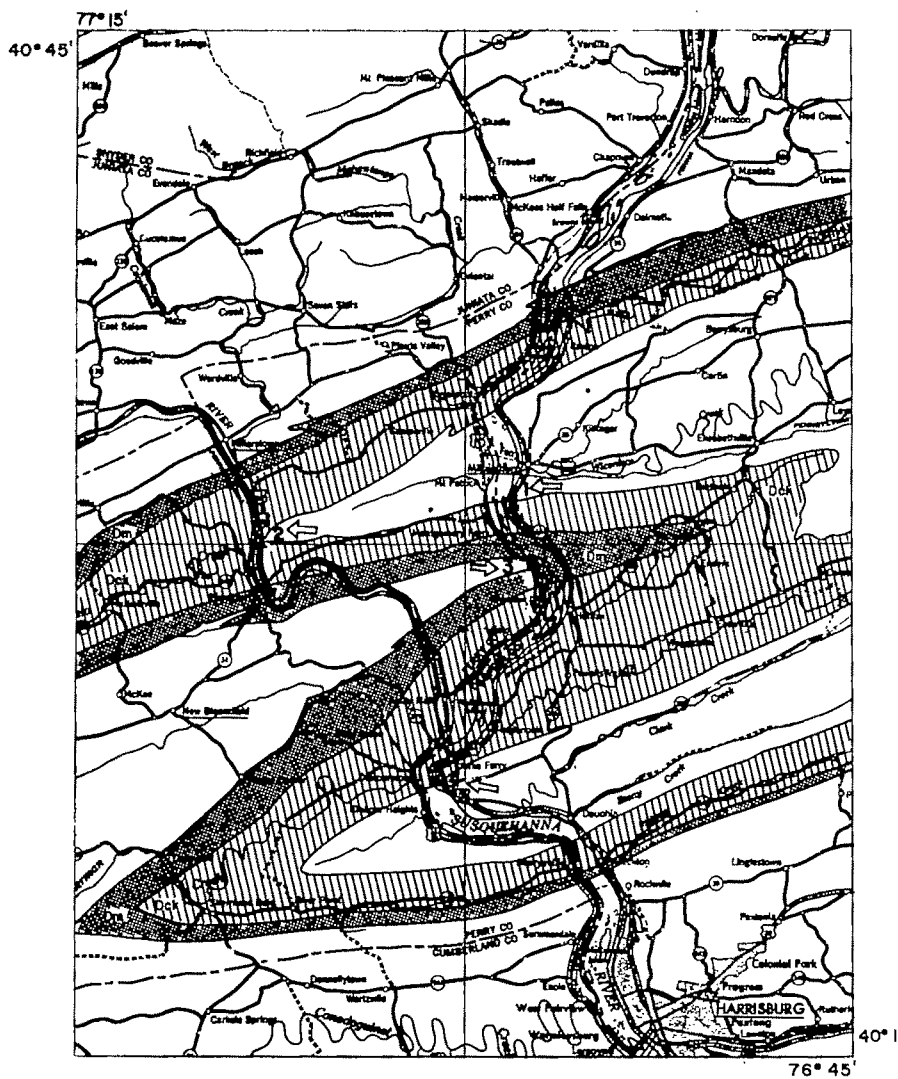


Fig. 3. Schematic cross sections showing two possible relationships between the Middle Devonian red beds of the Catskill Mountains in eastern New York and the Upper Devonian red beds of northeastern Pennsylvania.



LEGEND



Catskill Formation
(includes transition beds)



Upper Devonian Marine

MILLERTOWN - 15' quadrangle name

Fig. 2. Location of Susquehanna Group sections.

but the term that he submitted seems appropriate for current needs, and it is here proposed that the name Susquehanna Group be defined to include all rock units in Pennsylvania between the top of the red beds of the Catskill Formation and the top of the Hamilton Group.

GROUP SUBDIVISION

The generalized lithologic sequence of the Susquehanna Group consists of three fundamental units (fig. 1). Regionally, from east to west, and in local section from top to bottom the Susquehanna Group grades from dominantly nonmarine, to brackish, to dominantly marine sediments. Thus the group is logically subdivided into three major units: (1) an upper, mostly red, nonmarine unit, best developed in northeastern Pennsylvania, (2) an intermediate red and gray transitional unit, and (3) a lower, gray, marine unit, dominant in western Pennsylvania. It is expected that as work progresses the Susquehanna Group will be subdivided into many formations to accommodate local variations within the group.

Nonmarine unit.—The nonmarine unit of the group is the Catskill Formation. It consists of all the rocks between the base of the oldest major red unit and the top of the youngest, locally mappable red bed, and as thus defined comprises the bulk of the Devonian red beds. Some thick gray units are included within the Catskill Formation (fig. 1) in some areas, and for purposes of correlation these should be given member rank. The thickness of the formation in the Susquehanna Valley is approximately 3500 feet.

Transition unit.—The middle unit, for which there is no satisfactory unit name, will be named from a locality within the group type area. In the past, the term "Chemung", and to some extent the term "Portage", have been applied to various portions of this part of the section, one which includes all rocks between the Catskill Formation and the lowest, mappable red unit within the group. The approximate thickness of the transition unit in the Susquehanna Valley is 1500 feet.

Marine unit.—The lower or gray marine unit will be named from the Susquehanna Valley where it is best exposed, or the currently used local names proposed by Willard, such as the Fort Littleton and Rush (1935, p. 1199) formations, can be retained and redefined to include all rocks between the transition unit and the underlying Hamilton Group. The approximate thickness of the marine unit in the Susquehanna Valley is 2500 feet.

TYPE AREA

Central Pennsylvania, especially along the Susquehanna and Juniata rivers, provides an excellent median locality where all three major units are present and well exposed. There are no complete continuous exposures because the group is of the order of 7500 feet thick. However, a representative composite section can be compiled from the type area (fig. 2).

The local stratigraphy of the Susquehanna Group in central Pennsylvania can be determined from three roadcut exposures, which constitute a composite section north of the confluence of the Susquehanna and Juniata rivers. Section #1 (fig. 2), south of Millersburg on the east side of the Susquehanna River,

There is a need in Pennsylvania for a centrally located standard section of the Upper Devonian rock units to which local units can be referred and compared. A well-exposed, thick sequence of Upper Devonian units in the Susquehanna Valley region appears to be well suited as a type section. Current local studies in the central part of the state will be used to add units to the known framework of major and minor rock units which can be extended from that area throughout the state, eventually correlating with specific rock and time units in New York.

Many of the lithologic units in northeastern Pennsylvania proposed first by White (1881, 1882) and later modified by Willard (1939), as well as units in northwestern Pennsylvania proposed by Caster (1934), will be incorporated, if possible, as subdivisions of the new group. Within these and similar limited areas the vertical sequence of units within the group is already established. However, the physical continuity and intertonguing relationships of these and other units must be established by lateral tracing.

GROUP PROPOSED

Ashley (1923) proposed the term *Susquehanna Series* for the Upper Devonian units of Pennsylvania, which included the Catskill Formation at the top and the Tully Limestone at the base. Ashley's suggestion was not adopted,

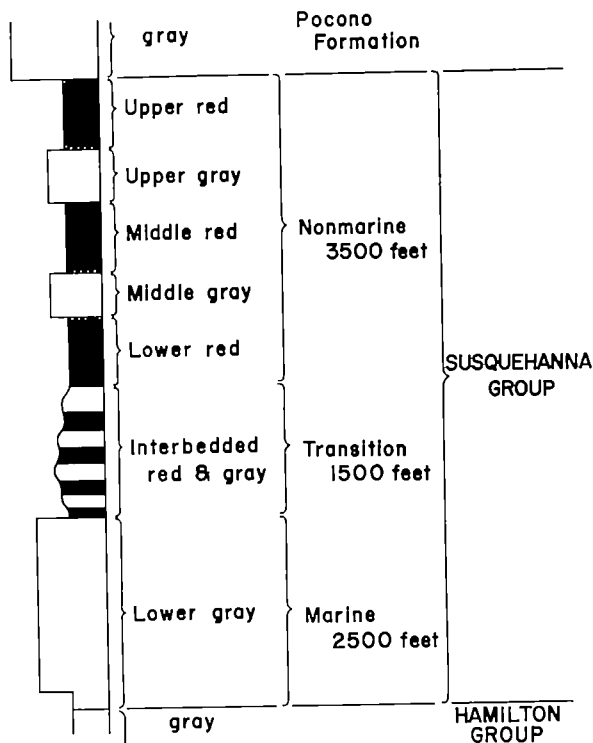


Fig. 1. Representative composite section of the Susquehanna Group in Dauphin and Perry Counties.

UPPER DEVONIAN ROCK STRATIGRAPHIC NOMENCLATURE IN PENNSYLVANIA

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ABSTRACT. The obvious inadequacies of the Upper Devonian terminology of Pennsylvania are the lack of a unifying rock term for the lithologic framework, as well as the lack of rock terms for the fundamental units within the framework. Recent work has made these inadequacies increasingly apparent. The name *Susquehanna Group* is proposed to include all rocks between the top of the red beds of the Catskill Formation and the top of the Hamilton Group. Definition of the units within the group is arbitrary and somewhat problematic because of areas of incomplete data, but through discussion with people working in this portion of the section it is hoped that a practical and utilitarian group subdivision will be made.

INTRODUCTION

The purpose of this paper is to propose a group name and to encourage new thought regarding the Upper Devonian stratigraphy of Pennsylvania. The members of the Pennsylvania Geologic Survey believe that the current nomenclature of the Upper Devonian in Pennsylvania is inadequate. This opinion stems from recent, detailed, field work as well as from problems that became apparent during the compilation of a new geologic map of the state. Much has been written about the Upper Devonian of Pennsylvania, but it is believed that a major nomenclatural framework must be established in order to integrate known and newly determined lithologic details. A detailed three-dimensional perspective of both lithologic and related paleontologic units will contribute significantly to the assimilation of detailed studies in progress and to the resolution of chronologic problems.

In the late 1800's the 2nd Geological Survey of Pennsylvania borrowed from the New York "standard section" names such as Genesee, Portage, Chemung, and Catskill to subdivide the Upper Devonian in Pennsylvania. As knowledge became more detailed in Pennsylvania, local terms were used as whole or partial substitutes of the early names. In recent years two factors have complicated usage of the original New York nomenclature: (1) New York geologists have gradually abandoned Chemung (Greiner, 1957, p. 8) and Portage as rock terms and (2) increased knowledge of Upper Devonian facies relationships in Pennsylvania has shown the necessity of establishing well-defined, time-transgressive rock units. Many geologists working in Pennsylvania, though aware of the gradual abandonment of the original names, continue to use them both in oral discussions and in print because of the lack of desirable alternate terms.

The relationship of the Upper Devonian stratigraphy of the northeastern and north-central parts of Pennsylvania to that of central Pennsylvania still presents unsolved facies problems. This northern area has always been the main obstacle to tracing of rock units laterally between known sections in New York and those to the south. During the early days of regional reconnaissance geology approximate correlations of the major units were defined; however, the details of the lithologic section in central Pennsylvania cannot be analyzed using comparative sections as remote as those in New York.

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U.S.S.R. The difference must be ascribed both to the considerable differences in latitudes between the areas concerned, and to the effects on the climate and periglacial survival of plants of the glaciated montane regions of central Europe, with their predominantly east-west orientation. The first of these in particular may be the reason for the admixture of the relatively thermophilous deciduous trees seen in the late-glacial pollen diagrams of the Midwest.

TABLE 1

Pollen sample from three amalgamated moss polsters in spruce-oak open woodland south of Highway I, northwest of Melbourne, Manitoba

	Number of grains	Percentage of total pollen
<i>Picea glauca</i> type	60	17.4
<i>P. mariana</i> type	5	1.5
<i>Pinus banksiana</i> type	53	15.4
<i>P. strobus-resinosa</i> type	6	1.7
<i>Ulmus</i>	2	0.6
<i>Quercus</i>	48	14.0
<i>Fraxinus</i>	1	0.3
<i>Betula</i>	41	12.0
<i>Alnus</i>	8	2.3
Total trees	224	65.2
<i>Corylus</i>	2	0.6
<i>Salix</i>	5	1.5
<i>Thuja-Juniperus</i>	2	0.6
Total shrubs	9	2.7
Gramineae	10	2.9
Cyperaceae	4	1.2
<i>Ambrosia</i>	27	7.9
<i>Artemisia</i>	35	10.2
Caryophyllaceae	1	0.3
Chenopodiaceae	26	7.5
Compositae	7	2.0
Rubiaceae	1	0.3
Total herbs	111	32.3
Total pollen	344	
Filicales	1	0.3
<i>Sphagnum</i>	1	0.3
<i>Selaginella rupestris</i>		very abundant, local in polster

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carr where the boring was made *Alnus* was common. Second, there is the fall in tree pollen, especially that of *Tsuga*, and the rise in NAP, shown by the curves of the pollen of Gramineae, Cyperaceae, and *Ambrosia*. The NAP rise must be associated with the settlement of the land and clearance of the Lake Forest in the region.

COMPARISONS OF THE LATE-GLACIAL

In the East of North America late-glacial conditions have been studied rather extensively. In northern Maine (Deevey, 1951) and Nova Scotia (Livingstone and Livingstone, 1958) the late-glacial diagrams show high proportions of NAP suggesting, according to Deevey (1958), the presence of tundra or park-tundra throughout the late-glacial (using our previous definition for this term). Farther south, in Connecticut for example, throughout the period correlated with the post-Cary to Valders time, forests with spruce are found (developing soon after a short NAP phase (Davis, 1958)). It therefore appears that a belt of open vegetation existed throughout late-glacial time outside the ice. On the other hand, in the Midwest we have shown that *Picea* forest and woodland are characteristic of the late-glacial within a few miles of the Valders maximum. The difference in the late-glacial climate in the two areas must largely account for the differences in vegetation; the continental Midwest climate allowing the growth of trees near the ice (also indicated by the frequent finds of logs in the till), and the oceanic climate in the East favoring the development of more open vegetation. A similar present-day effect is seen in the extension of the tundra zone southwards along the coast of Labrador. Another notable difference seen between the late-glacial pollen diagrams of the East and the Midwest is the higher proportion of *Artemisia* in the West and higher proportion of Ericales pollen in the East. This effect must also be related to the continentality in the West and the oceanicity in the East.

The late-glacial differences in North America are similar to trends seen in the European late-glacial (here using the term to cover the Lower Dryas, Allerød, and Upper Dryas Zones supposed to be correlated with post-Cary to Valders time): first, the broad zone of open vegetation of northwest Europe compared with the east in the U.S.S.R., where forest with *Picea* approached closer to the ice (Katz, 1957)—this is the kind of effect postulated by those who have studied the European climatic belts during the Last Glaciation (Büdel, 1951); second, the fact that in the late-glacial Ericales pollen is more abundant in the oceanic west, whereas *Artemisia* is more common in the more continental regions eastwards (Firbas, 1949). Here another similarity between the east of Europe and the Midwest late-glacial may be pointed out. This is the difficulty of finding Valders oscillations in the pollen diagrams of the Midwest; in the Russian Plain the Upper Dryas (Zone 3) period is unpronounced (Lisitsyna, 1959).

Thus these general trends in each continent are similar. In several respects, however, there are obvious differences, and here we may point out one of them. This is the greater area of open vegetation in northwest Europe in late-glacial times compared with that in eastern America, and similarly, the forest much closer to the ice in the Midwest than in the northwest of the

ice favored *P. strobus-resinosa* rather than *P. banksiana*, whereas the sandy soils in the region of Disterhaft's Farm Bog favored *P. banksiana*. A similar effect dependent on soil variation was described by Wilson (1938) in northern Wisconsin.

Ulmus, *Quercus*, and *Ostrya-Carpinus* percentages rise throughout this zone, and *Acer* is well represented. The NAP values fall to a minimum, as at the similar level in Disterhaft's Farm Bog, but they stay low, unlike their behavior at the other site. The forest remained closed in this region, whereas on the other side of the tension zone the influence of drier and warmer climates is seen in a higher NAP representation.

At the beginning of this zone inorganic sedimentation falls to a low level. But it suddenly increases in the middle of the zone at 523 to 540 cm. This change is accompanied by changes in the pollen spectra. The junction between the top of the sandy layer and the overlying detritus mud is very sharp. Two samples half a centimeter apart, one above and one below the junction, show the sudden change from high to very low *Picea*, as seen in the pollen diagram at 523 cm. The sudden recurrence of *Picea* is accompanied by increases in other pollen types common in zone 4, e.g. Gramineae, Cyperaceae, *Artemisia*. These sudden pollen and sediment changes indicate that in the time of zone 5 the lake level was lowered, zone 4 deposits exposed at the edge of the lake were re-worked, and their pollen was secondarily deposited together with inorganic material in the shrunken lake. The eroded state of the pollen immediately below the inorganic layer (sample at 550 cm) suggests a period of complete drying out and weathering at one stage. Possibly some of the higher NAP content results from growth of herbs on the surrounding surfaces bared by a lowering of the lake level. The rise in water level after the desiccation resulted in the resumption of the kind of sedimentation of pollen and sediment seen below the inorganic layer. The increase in pollen of *Pinus strobus-resinosa*-type and *Betula* immediately above the inorganic layer suggests that these trees were favored by the local environment changes accompanying the drying out. It is possible that the drying-out phase is a consequence of the lowered level (to 230 ft above sealevel) of Lake Michigan during the Chippewa Stage. At present, Seidel Lake (altitude 691 ft above sealevel) is only a mile from the coast of Lake Michigan, so the regional water levels must have been affected by the fall in the Chippewa Stage.

Zone 6.—*Pinus* falls to a minimum during this zone, and *Quercus* and *Acer* reach their maximum values. *Fagus* first becomes prominent in this zone. The NAP curve remains low.

Zone 7.—In this zone *Pinus* pollen again becomes dominant, and the percentages of *Ulmus*, *Quercus*, and *Ostrya-Carpinus* fall.

Zone 8.—In this zone *Pinus*, *Ulmus*, *Quercus*, and *Fagus* pollen percentages remain much as in the previous zone, but in addition the *Betula* percentages are higher and *Tsuga* first appears in quantity, reaching 26 percent of the total pollen at the top of the zone. Thus during the time of this zone it appears that the modern Lake Forest became established.

Zone 9.—In the final zone, two effects are discernible. First, the increase of *Alnus* as the lake sediment changes to a mossy telmatic deposit; in the shrub

Zone 7.—At the beginning of this zone the pollen percentages of *Ulmus* and *Ostrya-Carpinus* fall, as do those of other hardwoods such as *Carya* and *Juglans*. *Quercus* remains the dominant pollen type. The NAP rises to a maximum in this zone, with Gramineae, Cyperaceae, and Compositae playing the most important role. Does the NAP rise indicate the spread of prairie vegetation during the so-called Xerothermic Period? This is possible. The concomitant decrease of *Ulmus* and *Ostrya-Carpinus* may also indicate a change to drier conditions. Another interpretation is that it represents a local change in vegetation following the development of the hydrosere. Pollen of the rooted floating-leaf water plant *Brasenia* is common in this zone (the seeds were also found here), and the phase precedes the beginning of bog development seen in the succeeding zone. The increase in the grasses and sedges may reflect an increase of such plants growing round the edge of the shallowing lake.

Zone 8.—*Quercus* and *Pinus (strob-us-resinosa)* type) remain the dominant pollen types in this zone, as they were in the previous zone. Zone 8 is separated from zone 7 by vegetational changes probably local, that is, those following the development of the bog from the lake as indicated by the changes in sediment type at this level. The notable changes are the increase of *Betula* and Ericaceous pollen and *Sphagnum* spores and the decrease of the pollen of the Gramineae and Cyperaceae. Curtis (1959) describes the widespread occurrence of oak savanna in this part of Wisconsin in presettlement times. The high *Quercus* percentages must reflect this vegetation type, but it might be expected that NAP values would be higher than those found. The representation of *Pinus strob-us-resinosa*-type is presumably due to the fact that the site lies near the tension zone, where, and farther north, these pines play a more important part in the vegetation. Certainly the *Pinus strob-us-resinosa* percentages here are lower than those found in the later stages of Seidel Lake, on the northern side of the tension zone. The similarity of the pollen spectra from the base of zone 7 upwards suggests the oak savanna had an early origin.

Seidel Lake

Zone 4.—This zone is characterized by high values of *Picea*, mostly *P. glauca*-type. *Quercus* is the most common deciduous tree represented, as in zone 4 at Disterhaft's Farm Bog. *Ulmus*, *Ostrya-Carpinus*, and *Betula* occur in low frequencies. The NAP total is high, about 30 percent of the total pollen; it is composed mostly of Gramineae, Cyperaceae, *Ambrosia*, and *Artemisia* pollen. The zone represents the first vegetation of the area after the retreat of the Valders ice. This appears to have been open *Picea* woodland of the same type as was present during zone 3 outside the Valders ice. It is presumably contemporaneous with the closed spruce forest of zone 4 at Disterhaft's Farm Bog. In this instance it is clear that the open *Picea* woodland is a successional stage rather than one determined by climate.

Zone 5.—At Seidel Lake no closed *Picea* forest phase is present, and the *Picea* woodland disappears, to be replaced in zone 5 by *Pinus*, whose pollen is dominant throughout the time of the zone. It is mostly *P. strob-us-resinosa* type. There appears to be no *P. banksiana*-dominated period, as there was at Disterhaft's Farm Bog. Probably the clay soils left by the retreat of the Valders

Readvance must have had a direct climatic effect on the vegetation surrounding it, apart from regional climatic changes which led to the re-expansion of the ice sheet. Apart from a general cooling resulting from the proximity of the ice, it might be expected that the drying katabatic winds generated, even if infrequent, would discourage tree growth (Flohn (1953) suggests an influence of such winds on temperature relations beyond the ice sheet up to 50 to 100 km away). The result would be the development of more open vegetation in exposed positions. Such an effect might well help to explain the vegetational changes seen on the transition from zone 2 to zone 3.

Postglacial Vegetational History

It is not intended to give any detailed account here of the postglacial vegetational changes that reflect the amelioration of the climate as the ice retreated. The outline of the changes at Disterhaft's Farm Bog and at Seidel Lake will be given separately. After zone 4 the numerical zonations are independent and do not imply correlation.

Disterhaft's Farm Bog

Zone 4.—This is a *Picea*-dominant phase following the late-glacial. Just as a *Picea* forest appeared in the region after the retreat from the Green Lake Moraine in the Two Creeks Interval, so did this tree spread on the retreat of the Valders ice. The increase is of *P. glauca*-type pollen only. The NAP values, particularly *Artemisia*, remain high throughout the zone. Probably this pollen came from the open communities with *Artemisia*, which occurred 10 miles or more eastwards on the new soils in the area vacated by the Valders ice (see zone 4 at Seidel Lake). The course of the NAP curve at the transition between zones 3 and 4 indicates that *Picea* began to spread as the Valders ice melted, giving the NAP minimum. When the pioneer vegetation began to occupy the new Valders soils, the NAP rose again.

Besides *Picea* the only other prominent tree is *Quercus*, the percentages of which rise slightly throughout the zone. The low values of *Betula* also rise slightly here. Soon after the beginning of the zone, sedimentation becomes more organic and the high sandy content of the late-glacial sediments is much diminished.

Zone 5.—In this zone the pollen is dominated by *Pinus*, which completely replaces *Picea*. The *Pinus* pollen is mostly of the *P. banksiana* type. *Ulmus*, *Quercus*, and *Ostrya-Carpinus* percentages rise and the NAP curve falls to a minimum at the beginning of the zone. Probably the spread of *Pinus* in the region eliminated the open communities formerly colonizing the Valders soils, resulting in the NAP drop seen in this zone. It is clear that forest dominated by *Pinus*, particularly *P. banksiana*, was widespread in the region, whereas the deciduous trees spread more slowly.

Zone 6.—The high values of *Pinus* fall, and *Quercus* rises in this zone. *P. banksiana* pollen falls to lower values and is replaced by *P. strobus-resinosa*-type. The hardwoods *Ulmus*, *Ostrya-Carpinus*, *Carya*, *Juglans*, and *Tilia* are at their most frequent in this zone and in the latter part of the previous zone. The NAP values, mostly Gramineae and *Ambrosia*, rise slightly throughout the zone.

by many factors, of which dryness is an important one in the Midwest. The presence of *Ambrosia*-type pollen may have climatic significance. The pollen grains of the *Ambrosiaceae* have been described at length by Wodehouse (1935). The grains found fossil in this study closely resemble those of *Ambrosia*. This genus is characteristically found in the temperate and warm temperate regions of North America, and its presence indicates a warmer climate than might be suggested by the frequencies of *Picea* pollen. Such a climate would certainly not be one now associated with cold steppe (tundra) or cold wood-steppe (taiga).

Next must be discussed the causes of the change from the zone 2 forest to the zone 3 open woodland. It might be considered that this was a normal result of a climatic deterioration, the boreal closed forest being replaced by the more northern and open woodland, as happens in the zonation of the divisions of the boreal forest (e.g. the description of the zonal divisions of the boreal forest by Hare (1950)). If this simple explanation were correct, and we compared the climates governing the distribution of the two boreal forest divisions concerned according to Hare (1950), a fall in potential evapotranspiration from about 18 in. to 14 in. would be implied; or in terms of July °C temperatures, a drop of about 2.3°C from 12°C.

This boreal open woodland also occurs in more southerly places under conditions of poor water supply on dry soils. In the north, Hare suggests that there is physiological drought resulting from frozen soils during the period of maximum tree growth. Competition for available moisture would affect the trees more than the herbs, and spacing of trees would result. In the same way does summer drought seem responsible for the thinning of the boreal forest southwards in central Canada, as, for example, in the spacing of the trees in the open woodland area in southern Manitoba already referred to. As mentioned later, wind is another factor that might affect the forest/woodland balance by enhancing drought. In the case of the climatic deterioration associated with the Valders Readvance, it seems more reasonable to suppose that drought was due to frozen soils rather than to an absolute deficit of water. On the other hand, we have to consider the fact of the presence of deciduous trees and *Ambrosia* in the late-glacial pollen diagrams. Either this pollen is distantly derived, a possibility discussed in a previous section, or the spruce woodland is confined to severer upland habitats than the "warmer", perhaps riverine, element, in the same way that the cold steppe (tundra) and the boreal woodland interdigitate along the boundary between them, with the cold steppe on the uplands and the woodland along the rivers. It is unfortunate that the late-glacial species of *Artemisia* are unknown. Some species extend into the arctic. Others are associated with prairie or desert conditions. All seem to be associated with dry habitats. The high percentages of *Artemisia* pollen seen in zone 3 certainly indicate dry conditions. Perhaps they also indicate a frequency of the plant which might be associated more with warm steppe than with cold steppe conditions. On the other hand, the high zone 3 frequencies of *Picea mariana* may indicate the presence of lowland swamps.

Here must be suggested a more local reason for the reversion of the forest to woodland. The presence of the continental ice sheet of the Valders

(20)	Specific gravity of the glass constituting the two sliced portions (each =)	2.423
(21)	Specific gravity of complete hollow australite (determined in 1898)	1.06
(22)	Width of each half from plane of cut to edge of rim	28.5 mm
(23)	Total width of the two halves as measured from plane of cut to edges of rim	57.0 mm
(24)	Thickness of cut (= (1) - (23))	2.0 mm
(25)	Volume of internal cavity (from sum of volumes of caps of spheres)	49.91 cm ³
(26)	Calculated volume of glass lost by slicing (average of results obtained by two different methods)	1.39 cm ³
(27)	Volume of glass in complete hollow australite. (from $V = M/D$)	38.86 cm ³
(28)	Volume of complete hollow australite (from (25) + (27))	88.77 cm ³
(29)	Volume of complete hollow australite (from sum of volumes of caps of spheres using measured distances from poles to rim)	88.81 cm ³
(30)	Volume of complete hollow sphere before ablation (from $\frac{4}{3} \pi (R_B)^3$)	118.84 cm ³
(31)	Volume of glass in complete hollow sphere	68.93 cm ³
(32)	Volume lost by ablation (from (30) - (29))	30.03 cm ³
(33)	Volume lost by ablation (from (30) - (28))	30.07 cm ³
(34)	Aerodynamic heating (from $A.H. = \frac{k}{\sqrt{R_F}}$)	0.187
(35)	Percentage of glass lost by ablation of primary hollow sphere	43.6%
(36)	Percentage of volume lost by ablation of primary hollow sphere	25.0%
(37)	h_1 (= height of posterior half of internal cavity)	23.5 mm
(38)	h_2 (= height of anterior half of internal cavity)	23.5 mm
(39)	$h_1 + h_2$ = depth of internal cavity (from (37) + (38))	47.0 mm
(40)	d_1 (= height of posterior cap of australite measured from rear pole to rim)	23.5 mm
(41)	d_2 (= height of anterior cap of australite measured from front pole to rim)	30.0 mm
(42)	$d_1 + d_2$ = depth of hollow australite (from (40) + (41))	53.5 mm

The aerodynamic heating, which is inversely proportional to the radius of curvature of the front surface, is relatively low (0.187) and equal to only one-fifth the aerodynamic heating figure (0.92) obtained by averaging the calculations for 23 perfect flanged australite buttons of smaller size from the Port Campbell district of western Victoria. Complications arise with the hollow australites compared with australites that are solid glass throughout, because the smaller mass per unit frontal area of the hollow australites enables them

to radiate away a good portion of the aerodynamic heat input (*vide* D. R. Chapman, U. S. National Aeronautics and Space Administration); hence ablation would not be as great for hollow forms compared with solid forms of similar size and radii of curvature.

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THE BASEMENT ROCKS OF MALAYA AND THEIR PALEOGEOGRAPHIC SIGNIFICANCE IN SOUTH-EAST ASIA—A DISCUSSION

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In his paper in this JOURNAL (March, 1961) relating to Malayan paleogeography, Hutchison evidently has permitted his enthusiasm for publication to outweigh in several ways his sense of scientific discipline. Information on the geology of North Kelantan is now fairly complete, the result of detailed field-work throughout a period of nine years by MacDonald and Slater of the Geological Survey, Federation of Malaya. Hutchison's paper dealing with some of the rocks found in part of this area contains many inaccuracies and his conclusions are based on insufficient evidence. We therefore feel that this paper should not be allowed to pass unchallenged into the accepted literature on the geology of Malaya and that the following detailed discussion will help to clarify the problem.

HISTORY OF DISCOVERY AND MAPPING OF THE METAMORPHIC BELT OF NORTH KELANTAN

The Kelantan part of the 1948 Geological Map of Malaya, to which Hutchison refers (1961, p. 181), was compiled from data recorded by H. E. F. Savage and earlier geologists who made reconnaissance traverses in Kelantan in the early 1920's. The misinterpretation of the Kelantan schists at this time as being part of a thermal aureole is excusable in that only a small number of traverses were made across them and that numerous granite intrusions were encountered to the north of the Galas section.

The Kelantan schists were first recognized as unusual in the geology of Malaya by MacDonald who was Geologist, Kelantan, between 1951 and 1957. When Slater was posted to Kelantan in 1957 he agreed with MacDonald that these schists were of deepseated origin. Their northern limits by this time had been mapped by MacDonald, while Slater between 1957 and 1960 delineated their boundaries to the south, all on a scale of 1:63,360.

In postulating a deepseated derivation for these rocks, a certain amount of scepticism was encountered from other geologists in the Department, possibly because such an origin made them unique amongst the rocks of Malaya and because already they had been mapped as Carboniferous. However, in 1957 the section was shown to the late J. R. Paton, then Principal Geologist, who became convinced that they were products of regional metamorphism and probably part of a basement complex.

The following statement therefore appears on p. 2-J in the section on the geology of Malaya in Geological Survey Economic Bulletins, C-1.1, C-1.2, C-1.5, and C-1.6, published between December 1958 and April 1959:

"The only extensive body of schists discovered occurs in north Kelantan. Apparently it is not related to any of the known Mesozoic granites. It is overlain by

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shales which are thought to be Carboniferous or Permian, but there are no other pointers to its exact age. The schists may be either the metamorphosed equivalent of some of the Lower Palaeozoic rocks now known to occur in the Langkawi Islands off the west coast, or possibly may form part of the original basement complex. . . ."

Yet on p. 181 of his paper Hutchison says "To the writer's knowledge no published reference to this metamorphic belt exists." It should be noted further that the metamorphic belt lies some 100 miles to the east of the nearest lower Palaeozoic fossil locality, and not "immediately to the east", as stated on p. 182 of Hutchison's paper.

DESCRIPTION AND COMPARISON OF SCHISTS OF THE KELANTAN METAMORPHIC BELT

The Kelantan schists cover an area of almost 300 square miles, of which a little over 200 square miles were mapped by MacDonald and the rest by Slater. The schists are predominantly mica-garnet schist and quartz-mica-garnet schist in which occur bands of amphibole schist and narrower bands of quartz schist and of serpentine. Talc-carbonate schist is of rare occurrence. In addition to garnet, quartz, mica (often both muscovite and biotite), and feldspar, the mica schists commonly contain tourmaline and, in places, kyanite. Chlorite is often extensively developed, pyrite and graphite are occasionally prominent, and sillimanite and andalusite have been recorded. Concentrations of magnetite are present at a few localities in the mica schists, and in one case the magnetite occurs in a band of schistose skarn containing, in addition to the magnetite, amphibole (tremolite-actinolite partly altered to grunerite-cummingtonite), garnet, and apatite. Rutile is of very common occurrence associated with vein quartz, which occurs extensively throughout the schist sequence. Many of the quartz veins are auriferous.

Bands of amphibole schist occur at several localities, but their most extensive development is in the southern part of the schist belt where good exposures occur in the Sungei Galas. Pyroxene schist composed essentially of quartz, diopside, sphene, and plagioclase, and associated with the amphibole schist, is also exposed in the Sungei Galas. Clinozoisite and sphene are rather common in the amphibole schist and epidote occurs in places but is not particularly abundant. Cordierite has been recorded in a quartz-amphibole-garnet schist.

Hutchison states (1961, p. 181) that an attempt would be made to describe briefly the petrology of the rocks and their grade of metamorphism, but only the amphibole schists, which form but a small part of the whole sequence, are described. He also states that this belt of regionally metamorphosed rocks in Kelantan is of amphibolite grade, but again it is only a small portion of the belt, the amphibole schists, that have been so described.

Hutchison implies that the amphibolite facies is confined to the western part of the succession. In fact, lenses of hornblende schist occur throughout the sequence, interbedded with quartz-mica and garnet-mica schists, and can be seen near Kampong Berhala at the eastern end of the Galas section. The predominant amphibolite type is a hornblende-clinozoisite-andesine schist, containing as much as 30 percent clinozoisite, occasionally found with garnet or calcite.

It is astonishing to read further on p. 182 that in Malaya there are "several" metamorphic localities but "always of low grade", and that the Kelantan rocks of "amphibolite grade" are "unique in this respect". It is not practicable in this discussion to list all the published references to the numerous schist localities of both low and high grade (including amphibole, epidote, biotite, chlorite and graphitic schists) within Malaya, but the following statement indicates where these may be found.

Eight Geological Survey Memoirs, and a number of detailed reports, covering various districts of the States of Kedah, Perak, Selangor, Pahang, Negri Sembilan, Malacca, and Johore have been published and most of them are still in print. In the Memoirs alone there are more than 120 page references to schists in Perak, Selangor, and Pahang, and other reports describe schists and phyllites from most other parts of Malaya. In particular Richardson (1947) describes in detail amphibole schists from northwest Pahang containing actinolite, epidote, micas, chlorite, tremolite, anthophyllite, garnet, and pyroxene, and states (1947, p. 242) "The schists comprise alternating folia of dark and light components. Common combinations are bands predominantly of amphibole, quartz and amphibole, epidote and quartz, graphite veinlets, and so on. . . ."

NATURE OF CONTACT AND STRUCTURES OF THE KELANTAN METAMORPHIC BELT

The nature of the contact of the Kelantan metamorphic belt and the adjoining sedimentary rocks forms a difficult problem. No naturally exposed section of this contact has been discovered to date, but a large part of it is known to be complex and not a simple unconformity as Hutchison implies. Though pitting revealed a contact of mudstone and schist at one point on the banks of the Lebir River, the whole of the southern margin of the formation was observed to be a zone of minor igneous intrusion and intense shearing, resulting probably from movements of sedimentary/volcanic rocks of differing competency upon the schist surface during folding, whereas part of the eastern margin appears to have been faulted.

On p. 181 of his paper Hutchison states that the contacts of the belt of metamorphosed rocks with the Carboniferous sediments to the east and to the west are sharp and apparently unconformable. He is probably correct in saying that the sediments to the east are Carboniferous, but what evidence does he have for this statement?

Although the Kelantan schists appear to form an asymmetric anticline in the south, this is certainly not so in the north. Even in the south it is doubtful whether Hutchison could have discovered this from a traverse along the Galas section. He does not appear to have appreciated the fact that, in the south, the uniform folding of the schist sequence contrasts strongly with the isoclinal and contorted structures of the "Carboniferous" sediments overlying them and now outcropping to the east, west and south, nor, having attributed the arching of the metamorphic formation to the Early Paleozoic, does he attempt to explain how the sedimentary/volcanic rocks were so acutely folded without involving the schists. Had he carried out an effective program of field mapping he would almost certainly have formed the opinion that the parallelism of trends of the

Kelantan schist belt, the early Paleozoic formations, the Carboniferous and Triassic formations, not to mention the Main Range granite, results from their having been acted upon by the same compressional forces—those of Mesozoic time—and not necessarily from discontinuities of sedimentation alone.

THE PALEOZOIC ROCKS OF MALAYA

The map and its explanation (p. 182) are fanciful and misleading. The “extensions” of Cambrian and Ordovician-Silurian seas are extravagant, based, as they are, entirely on a few isolated localities over 100 miles apart, and to say on p. 184 that they “. . . . can be constructed with a fair degree of certainty. . . .” is absurd.

Hutchison mentions also on p. 184 the discovery of Ordovician and Silurian fossils in Perlis, of Cambrian fossils on Terutau and Langkawi, and of “graptolite-bearing Ordovician-Silurian” rocks at Kuala Lumpur, but since he makes no reference to, or acknowledgment of, the published reports by Jones (1957), Kobayashi (1957, 1958, 1959, 1960), and many others, it would appear that he has not seen them. No graptolite-bearing rocks are known at present from the vicinity of Kuala Lumpur and it is presumed that he has misreported the discovery by Geological Survey staff in 1957 of limestone near Kuala Lumpur containing Middle and Upper Silurian brachiopods, corals, and gastropods identified by C. P. Nuttall, H. Dighton Thomas, and S. Ware of the British Museum of Natural History.

He furthermore states categorically (p. 182 and 184) “Devonian is entirely absent from the area.”; “No Cambrian exists to the south of North Malaya.”; “No rocks of similar [Ordovician-Silurian] age exist to the south of Malaya.” Such statements are pure suppositions and quite premature.

PALEOGEOGRAPHY IN SOUTH-EAST ASIA

Hutchison makes little reference to the more recent papers (Jones, 1957; Kobayashi, 1960; Krishnan, 1960, p. 67, 162-165) in this connexion. On p. 184 of his paper he says of the “Archean Mongok gneisses” “. . . . “The Burmese Precambrian is on the same strike as the Malayan basement ridge described here”, when in fact the Mogok (not Mongok) gneisses at Moulmein, their nearest approach to Kelantan, are some 800 miles to the north-northeast across the Isthmus of Kra. The Geological Map of Thailand (Brown and others, 1951) shows no continuation of these rocks through the Isthmus of Kra and there is no apparent correlation with Kelantan.

Concerning the Mogok portion of the Stone Tract (Iyer, 1953, p. 13-26, 38-42, 79), Chhibber (1934), quoted by Hutchison, in fact says on p. 126 quoting Fermor (1931, p. 85):

“The general grade of metamorphism of the rocks of these areas as represented by their mineral contents, appears to me to refer the whole of these rocks to the hypomorph zone This is indicated at once by the fact that certain minerals, at least in the rocks collected by me, are conspicuous by their absence. The most important of these absent minerals are epidote, green hornblende, staurolite, kyanite, chlorite, sericite, and muscovite (except in a single case) and microcline.”

Of these minerals specifically excluded by Fermor, staurolite, kyanite, chlorite, muscovite, (and green hornblende and microcline?) have all been identified

by MacDonald and Slater from various parts of the Kelantan schist belt. What mineralogical correlation or similarity can possibly be invoked?

In his conclusion on p. 183 Hutchison gives as one of the reasons for the Precambrian age of the metamorphic rocks of northeastern Malaya the fact that their mineralogy suggests an igneous origin. It is agreed that the amphibole schists are almost certainly of igneous origin and derived from volcanic rocks, but the amphibole schists form only a small part of the Kelantan schist sequence, the greater part of which is without doubt of sedimentary origin. In any case the fact that the amphibole schists are of igneous origin can hardly be given as a reason for their age being Precambrian (cf. Richardson, 1947).

It has been stated above that the nature of the contact is not simple and that whereas in some places it may appear to be a single unconformity it is not so elsewhere. The balance of evidence appears to indicate shearing in the south and, in some places on the eastern margin, faulting. Though it is agreed that the probable age of the Kelantan schists is Precambrian, none of the evidence adduced by Hutchison in support can be regarded as valid.

Lastly, but by no means least, Hutchison does a disservice to Malayan geology by perpetuating a view that the emplacement of the Malayan granite and the folding and minor metamorphism of the main sedimentary successions are Tertiary. Sufficient evidence has now been accumulated to indicate that the bulk of these events occurred during Jurassic times.

CONCLUSION

Even assuming the geology of the Malay Peninsula to be as simple as Hutchison apparently imagines, he should be aware that a paleogeographic map cannot be taken seriously if based only on three completely isolated areas containing fossils, insignificant fieldwork, and scraps of unacknowledged information, and that such vast and partly erroneous inferences drawn from such paucity of data can neither advance a proper understanding of the geology of Malaya nor satisfy "a need of long standing". It is difficult to understand how anyone in his position as a senior lecturer at a University intending to write a paper on any aspect of the geology of Malaya should do so without first making a proper study of the available literature or officially seeking information from its main repository, which is the Government Geological Survey. As a result of informal discussions with Slater it was certainly known to Hutchison that both MacDonald and Slater had spent many years working in North Kelantan and that the rocks there had been accurately mapped by them by the time his paper was being written. Hutchison must have been aware that such information, although still not completely prepared for publication, would have been made available to him had he made a formal request for it and that he could have used it provided he acknowledged its source.

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THE BASEMENT ROCKS OF MALAYA AND THEIR PALEO GEOGRAPHIC SIGNIFICANCE IN SOUTH-EAST ASIA—A REPLY

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In their discussion of my recent article, Alexander, MacDonald, and Slater have made several accusations which I must hasten to refute. The writers have assigned themselves the powers not only of commenting on the geological content of my article but also on the author's "sense of scientific discipline" in their introduction. Comment on the geological content of my paper is indeed welcome, but references to the author's character are deplorable and exhibit irresponsibility on the part of the writers. It is hard to see what they had hoped to gain by this.

The writers give as the reason for their discussion that my references to the rocks in North East Malaya are partly inaccurate and my conclusions based on insufficient evidence. They make this bold introductory statement without at any subsequent stage producing definite corroboration. The few attempts made by Alexander, MacDonald, and Slater in this respect can easily be refuted, as, for example:

In the last paragraph of "History of Discovery, etc." Alexander et al. state: "Yet on p. 181 of his paper Hutchison says 'To the writer's knowledge, no published reference to this metamorphic belt exists', implying thereby that I had not read the obscure reference Federation Malaya Geol. Survey Econ. Bulls., C-1.1, C-1.2, C-1.5, and C-1.6, p. 2F-2K, published between December,

1958 and April, 1959. It is hardly surprising that I have never seen this reference of complex coding and dating. It is interesting, however, that Alexander et al. made no reference to the more recent publication by Alexander, Paton, and Jones (1959). I made reference to this paper in my original article and pointed out that in it Alexander made no mention of the N. E. Malayan metamorphic rocks. It is strange that in the discussion he should not include or refer to this most recent relevant work of wide circulation, but instead refer back to an obscure publication of localized circulation.

In the third paragraph of "Description and Comparison of Schists . . ." Alexander et al. write: ". . . but only the amphibole schists, which form but a small part of the whole sequence, are described". On page 182 of my paper I clearly stated that the metamorphic complex is largely of garnetiferous mica schist. At no time did I imply that the metamorphic belt is largely or only of amphibolite. I stated quite clearly that I was concerned only with the amphibolite, and at no time did I attempt to describe fully the rest of the metamorphic complex. Alexander, MacDonald, and Slater continue: "Hutchison implies that the amphibolite facies is confined to the western part of the succession". What I in fact said is: "Of particular interest is the western part of the succession, which is amphibolite facies". There is certainly no such implication in my statement. I am quite well aware that there are lenses of amphibolite throughout the sequence.

The writers of the discussion have criticized my statement that there are several localities of metamorphism in Malaya, but always of low grade. They hold the opposite view and go on to list eight geological memoirs and to count the number of pages (at least 120) which have been written on "schists" in Malaya. I gave the impression on page 182 of my article that metamorphic rocks are by no means abundant in other parts of Malaya, but Alexander et al. would have us believe this is untrue and would suggest that the abundance is in the ratio of the number of pages written about them. This surely cannot be taken as a serious criterion. I have reread the memoirs referred to by Alexander et al. but still maintain the opinion I stated initially that there are several localities but always of low grade. Nowhere have I seen reference to high grade metamorphic rocks. The example which the writers themselves quote in the last paragraph from Richardson (1947) of amphibole schists containing actinolite, epidote, micas, chlorite, etc., which show common combination of bands of amphibole, epidote, and graphite strongly suggests that the rocks should generally be ascribed to the Albite-Epidote Hornfels facies resulting from contact metamorphism by the main granitic batholith. As an upper limit they could possibly be ascribed to the greenschist facies, but in either case they can generally be regarded as being caused by relatively low temperature and pressure.

This example given by Alexander, MacDonald, and Slater supports my statement that other metamorphic localities in Malaya are of low grade. The writers of the discussion seem to be unaware of the distinction between low and high grade metamorphic facies and seem to be under the mistaken concept that amphibole and epidote necessarily indicate high grade conditions. I beg to draw their attention to an excellent summary of metamorphic reactions

(Fyfe, 1958). Richardson (1950), to whom the authors of the discussion made special reference, describes metamorphic rocks from N. W. Pahang as follows: "... composed of elongate actinolite crystals, alternating with lamellae of quartz-orthoclase aggregate, pyrite, epidote and chlorite and veins of calcite are common. . . .". These rocks, as in the case of all other metamorphic localities, are close to the granite contact. This again suggests a generally low grade of contact metamorphism, and from the memoir the orthoclase appears to be of detrital origin which may or may not have been recrystallized by contact metamorphism. Certainly the presence of orthoclase implies low pressure.

On reading through the Geological Survey memoirs, I have nowhere seen a description of a metamorphic locality that can be ascribed to a grade of regional metamorphism anywhere as high as the Almandine Amphibolite facies to which I ascribed the N. E. Malayan rock in which coexistence of andesine feldspar and epidote is highly characteristic. Fyfe, Turner, and Verhoogen (1958) attribute it to a high load pressure. This schist I have described is certainly unique in Malayan geology and is of a considerably higher grade of metamorphism than anything described from other parts of Malaya in Geological Survey publications to date.

I am not in a position to comment further on the nature of the contact and structure of the Kelantan metamorphic belt because, as mentioned in my paper, I spent only a short time in the area. It is interesting to learn that the detailed report of this area is now complete and I look forward eagerly to its publication.

My evidence for stating that the sediments to the east are Carboniferous is the 1:5,500,000 geological map of the Thai-Malay peninsula published in 1958, compiled by Alexander. The map states clearly that the sedimentary rocks of the area are "Younger Palaeozoic". I took this information from his map on its face value, but Alexander seems to question its validity.

The writers of the discussion appear to have completely missed the point of my short article and to have expected a complete and exhaustive field account of the structures of N.E. Malaya. This was obviously not my aim and I made it clear that "time spent in the locality did not permit a detailed structural analysis". From their discussion it now appears that the Geological Survey Officers have completed such an analysis.

I very much question the veracity of the last sentence of the section on "Nature of Contact and Structures . . .", which states that an effective program of field mapping would lead me to form the opinion that the parallel trends of the Schist Belt, the early Paleozoic formations, the Upper Paleozoic and the Mesozoic and the Main Range granites result from the fact that they have all been acted upon by the same compressional forces. From my observations of the Malayan Granite batholith, I have seen absolutely no evidence that it has been co-folded with the older sedimentary formations. On the contrary, my observations have led to the conclusion that the granite is discordant and in no way parallel in structure. In a forthcoming paper, I will demonstrate that the Malayan Granite has been discordantly intruded into Mesozoic sediments in Singapore Island and has effected a considerable metamorphism on the geosynclinal sediments. The structures of the latter are in no way concordant

with the granite. Since the writers of the discussion seem to be under a misapprehension, it appears to be necessary for me to repeat now my views regarding the parallelism of the lower Paleozoic rocks in Malaya. The anticlinal belt of metamorphic rocks represents the position of a structurally positive, or geanticlinal axis which, by fluctuating in level, has partly controlled the lower Paleozoic sedimentation. It would be foolish of me to say that subsequent compressional forces have not modified the outcrop pattern. The writers seem to have failed to appreciate the fact that I was attempting to reconstruct the paleogeography and not the outcrop patterns. The parallelism of the Cambrian and Ordovician extents must surely almost entirely be due to sedimentation, or would the writers have us believe otherwise, as they suggest in their discussion?

Such a bold statement as that which introduces the section "The Paleozoic Rocks" without any further discussion is itself "absurd". Admittedly, the determined fossil localities are at times over 100 miles apart, but the strata which contain these fossils are not isolated localities as the writers suggest. Stretching southwards along the west coast of Malaya is a predominantly limestone formation which on the 1948 map is shown as Carboniferous and on Alexander's 1958 map as Younger Palaeozoic with an isolated Older Palaeozoic locality at Kuala Lumpur and another at Kanthan and a large area in Langkawi and Perlis that extends continuously northwards into Thailand. The alluvial plain that extends along the west coast of Malaya is largely underlain by limestone at least as far south as Kuala Lumpur. The author is of the opinion that much of this is lower Paleozoic in age, even although the Geological Survey would hold it to be Carboniferous. It is surely equally absurd to interpret the outcrop pattern in any other way than I have done in my article. Surely the writers do not believe in isolated miniature lower Paleozoic basins, one at Kanthan and another further south near Kuala Lumpur. These must have been connected by an arm of the sea to the main sedimentation basin in the north. Jones (1957) attempted a similar paleogeographic interpretation but terminated his sea extensions just south of Langkawi, since at that time the more southerly fossil discoveries had not been made. Reinterpretation in the light of recent discoveries can hardly be dismissed as "absurd".

It is again strange that Alexander et al. should criticize me for not referring to an older publication when in fact a more recent and more up-to-date one exists, as, for example, they criticize me for making no reference to or acknowledgement of a paper by Jones (1957). I did in fact base my information (and acknowledged the fact) on a more recent paper by Jones on the same subject (1959). My article was in no way intended to include a historical review of the state of knowledge, as Alexander et al. seem to think.

I am grateful to Alexander, MacDonald, and Slater for a correction regarding the fossil content of the Silurian Rocks of the Kuala Lumpur area. Details of the fossil localities are not available to the public. My knowledge of the existence of the locality was taken from Alexander's map (1958) and I assumed, and it seems wrongly in this case, that the fossil content was similar to the other localities that have been published. A publication by the Geological Survey on this 1957 discovery would indeed be most welcome.

Regarding the writers' outright condemnation of my statements that there is no Devonian in Malaya, that no Cambrian exists to the south, that no Ordovician/Silurian exists to the south of Malaya, I would point out that these are not "pure suppositions and quite premature". They are based on a fair amount of evidence. In Perlis, for example, I have examined, below the bridge at Kaki Bukit, siltstones and sandstones of lower Carboniferous age. These beds directly overlie the Ordovician/Silurian limestone. Certainly in N.W. Malaya there is no evidence of Devonian in the succession, and Silurian appears to be directly overlain by Lower Carboniferous. For field information in the Perlis area I am grateful to C. R. Jones who surveyed the area five or six years ago. Unfortunately, for reasons unknown, publication of his memoir on Langkawi and Perlis has been held up by the Geological Survey; therefore, I cannot refer to published information which would support my statement that Devonian is absent from Malaya. As far as is presently known, no Cambrian exists to the south of North Malaya. My statement is not "supposition". No Ordovician/Silurian rocks have yet been described from the south of Malaya, either in Sarawak or Indonesia, both of which areas have been very well surveyed. For the writers to state that "such statements are pure suppositions and quite premature" implies that they have good reason to suspect that Devonian does exist in Malaya and that lower Paleozoic rocks do occur to the south of Malaya. It would be of general interest to enquire what reason they have for this suspicion.

Alexander et al. bring my attention in their section "Paleogeography . . ." to a recent publication of Krishnan (1960). However, they have obviously not read it themselves, as they go on to say that the nearest approach of the Mogok gneisses to Kelantan is at Moulmein, which is 800 miles across the Isthmus of Kra. The map in Krishnan (1960) clearly shows that these crystalline rocks extend along the strike as far as the Burmese Thailand border as isolated outcrops; in fact, the Geological Map of India (West, 1949) shows these isolated remnants of the Precambrian rocks extending into Thailand at the Isthmus of Kra. This is a distance of less than 400 miles from Kelantan. I have not seen the geological map of Thailand referred to by the writers, but am surprised to learn that it shows no outcrops of these metamorphic rocks in the Isthmus because they are quite numerous on the Burmese side of the boundary in this area.

The quotation from Chhibber (1934, p. 126) by Alexander et al. and their following conclusions or lack of conclusions regarding this peculiar process of mineralogical correlation, I fail to understand. It neither adds nor supports any argument on correlation. The absence of these minerals mentioned is not significant. One cannot apply the methods of paleontological correlation to metamorphic areas, as Alexander, MacDonald, and Slater have suggested.

The Mogok rocks of Burma "bear the impress of high grade metamorphism and have a typical Archaean aspect" (Krishnan, 1960). In this respect they are similar to the metamorphic rocks of Kelantan.

At no time in my article did I imply that the amphibole schists form anything but a small part of the sequence. It was clearly stated that the sequence

is largely of "garnetiferous mica schist with occasional psammitic bands" and hence of sedimentary origin. The fact that they are partly igneous in origin and have been metamorphosed to the high grade of Almandine Amphibolite facies was one of my reasons for suggesting a Precambrian age.

It is interesting and gratifying that Alexander et al. should agree with my conclusion that the probable age of the Kelantan schist is Precambrian. Since they regard none of my evidence as being valid, I look forward with expectation to the publication of the Geological Survey memoir to find on what evidence they do in fact deduce a Precambrian age.

In the last paragraph of "Paleogeography . . ." the orogenic folding associated with the granites is referred to as "minor"; yet when I made a similar reference in my article, the writers took great pains to invalidate my statement by quoting memoir references to the contrary. They further state that "sufficient evidence has now been accumulated to indicate that the bulk of these events occurred during Jurassic times". This evidence has not been made public as far as I am aware. I quote from several Geological Survey memoirs:

"Evidence from the Netherlands East Indies and Malaya combined indicates that the date of the intrusion lies between Upper Mesozoic and Upper Tertiary" (Savage, 1937).

"The granite is therefore Post Triassic, and from evidence elsewhere is believed to be of late Mesozoic age" (Ingham, 1938).

"The age of the intrusion is not definitely known; it may have been emplaced during the uppermost Mesozoic or Lower Tertiary epochs" (Richardson, 1939).

"Their exact age is unknown" (Richardson, 1950).

" . . . emplacement probably took place during the Cretaceous period but it may have occurred during the Upper Mesozoic or Lower Tertiary epochs" (Roe, 1951).

" . . . it is now acknowledged by most authors that the granite is . . . probably Cretaceous . . ." (Ingham and Bradford, 1960).

" . . . but they go on to state that the only definite age limitation is that the granite is known to have invaded and altered Triassic sediments" (Ingham and Bradford, 1960).

I have never seen published indisputable evidence to settle the question as to whether the granites of Malaya are Mesozoic or Tertiary, and the sooner the evidence which Alexander et al. refer to is published the better, as it will settle what has been a major controversy in this area. To simply say that "sufficient evidence has now been accumulated to indicate . . ." is no argument by itself.

The introductory sentence of the "Conclusion" of their discussion shows the emotional nature of the reaction of the writers to my article. It is difficult to appreciate what object they must have had in mind when they indulged in such an irresponsible and rather personal attack which is grossly unjustified and only serves to display their mental immaturity and instability. Their first sentence, for example, is based on the premise that I have shown from my paper that I believe the geology of Malaya to be "simple". This is far from

the truth, as any disinterested reader will have ascertained. In the article I was concerned only with the broader aspect of the paleogeography of the area. As explained earlier, my paleogeographic map was not based entirely on fossil localities. Their references to "insignificant field work, and scraps of unacknowledged information" are completely incomprehensible. My map was drawn on the basis of Geological Survey publications which I referred to in my article, and also on Alexander's map (1958) and a visit to Kelantan. The writers' reference to "insignificant fieldwork" must, therefore, be a reference to that of the Geological Survey, though I can hardly imagine this to have been their intention. No "unacknowledged information" was used in my article. If the writers feel that my interpretation of the paleogeography of Malaya is vastly erroneous, then I will indeed welcome an alternative interpretation, but an outright and unreasonable rejection such as they have made serves no purpose whatsoever. My paleogeographic map, I feel, presents the only interpretation possible on the present state of knowledge of Malaya. I at no time intended it to be the last word on the subject. If one were to delay publication constantly because of uncertainty and because of limited outcrops, according to the policy of the Geological Survey of Malaya, then no advancement or "proper understanding" would ever be envisaged. For example, as I noted earlier, publication of the memoir on N.W. Malaya by C. R. Jones has inexplicably been delayed by the Survey for at least five years.

Regarding the writers' criticism that I have referred to only a small portion of the total available literature, I have already indicated that it was not my aim to give a completely exhaustive geological report or to give a historical review of geological work in Malaya. I referred to some of the more recent publications. The writers seem to have referred to a much wider literature, but with little effect, as I have shown above. It can hardly be said that the statements made in their discussion indicate that they have made "a proper study of the available literature". Yet they have the temerity to accuse me of this particular failing. I wish furthermore to point out that I wrote this article as a private individual and in no way in the capacity or "position as a senior lecturer at a University", as the writers seem to think.

The second-last sentence of the writers' discussion takes me completely by surprise. This statement has brought to my notice for the first time the fact that MacDonald had been working in North Kelantan and also that the rocks had been accurately mapped by MacDonald and Slater by the time my paper was being written. I was indeed aware of the fact that Mr. Slater was the Field Geologist for Kelantan and was stationed in that State, just as I was aware of the fact that there was a State Geologist in nearly every other state in Malaya, from the extreme north to the south.

Their final sentence is completely irrelevant. As pointed out before, it was not my intention at any stage to write a detailed field report of the metamorphic rocks of Kelantan, but rather to deal only with their paleogeographic significance—a fact which is adequately clear from my article. Why, therefore, I should have wished to formally consult the Survey maps whose existence I was unaware of, is by no means clear to me. However it is a most welcome offer that the field reports of the Survey are available on application and may

be used in publication, provided acknowledgement is made. This service was unknown to me, but I shall bear it in mind should an occasion arise in the future.

Finally, allow me to thank Messrs. Alexander, MacDonald, and Slater for their criticisms of my paper and for drawing my attention to the few inaccuracies which I hope have now been cleared up. Permit me, however, in retrospect, to requote in a slightly altered form the writers' introductory sentence: "Alexander, MacDonald, and Slater have evidently permitted their enthusiasm for destructive and emotional criticism to outweigh in several ways their sense of reason and professional behavior".

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